CALIFORNIA
AIR RESOURCES BOARD

Standard Operating Procedure for the Determination of Selected Organophosphate Pesticides Collected on XAD-2 Resin by Gas Chromatography-Triple Quadrupole Mass Spectrometry

MLD077
Revision 0.0

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
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Standard Operating Procedure for the Determination of Selected Organophosphate Pesticides Collected on XAD-2 Resin by Gas Chromatography – Triple Quadrupole Mass Spectrometry

1. Scope

This SOP describes the analysis of eleven organophosphate pesticides in ambient air. These pesticides are Dichlorvos, Dimethoate Oxygen Analog (OA), Dimethoate, Diazinon OA, Diazinon, Malathion OA, Malathion, Chlorpyrifos OA, Chlorpyrifos, SSS-tributyl phosphorotrithioate (DEF) and Phosmet. Residues of these eleven compounds are extracted from XAD-2 using ethyl acetate and determination is made by gas chromatography – triple quadrupole mass spectrometry in the Selected Reaction Monitoring (SRM) mode. This SOP should be used in conjunction with the Northern Laboratory Branch's (NLB) Laboratory Quality Control Manual (QCM) and the instrument manufacturer operation and software manuals.

2. Summary of Method

Residues of selected pesticides are collected on XAD-2 resin tubes that are placed on a sampler for 24 hours at a flow rate of 1.0 liters per minute (L/min). The samples are stored in a freezer until extracted with 4.00 mL of residue grade or better of ethyl acetate. The extract is analyzed by a GC-MS/MS in the SRM mode. Sample analysis and quantitation uses an external standard method for instrument calibration.

3. Acronyms

Acronym or Term	Definition
CARB	California Air Resources Board
CAS	Chemical Abstracts Service
CCV	Continuing Calibration Verification
CS	Control Standard
DEF	SSS-tributyl phosphorotrithioate
DPR	Department of Pesticide Regulation
EQL	Estimated Quantitation Limit
eV	Electron Volts

Acronym or Term	Definition
GC-MS/MS	Gas Chromatography Triple Quadrupole Mass Spectrometry
H&SC	Health & Safety Coordinator
HPLC	High-Performance Liquid Chromatography
kPa	Kilopascal
LCS	Laboratory Control Spike
LIMS	Laboratory Information Management System
MDL	Method Detection Limit
MLD	Monitoring and Laboratory Division
m/z	Mass to Charge Ratio
ng/m^3	Nanograms per cubic meter
NLB	Northern Laboratory Branch
OA	Oxygen Analog
OLS	Organics Laboratory Section
PFTBA	Perfluorotributylamine
PTFE	Polytetrafluoroethylene
RL	Reporting Limit
QC	Quality Control
QCM	Quality Control Manual
RPD	Relative Percent Difference
SAS	Special Analysis Section
SDS	Safety Data Sheet
SOP	Standard Operating Procedure
SRM	Selected Reaction Monitoring
UHP	Ultra-High Purity

4. Definitions

4.1. ANALYTICAL BATCH – A set of prepared samples (i.e. extracts) analyzed together as a group in an uninterrupted sequence.

4.2. BLANK – Sample media, solvent, or reagent that has not been exposed to the sample stream in order to monitor contamination during sampling, transport, storage, extraction, or analysis. The blank is subjected to the same analytical processes as samples.

4.2.1. METHOD BLANK – An XAD-2 resin tube that is free of the analytes of interest. This tube is extracted in the same manner and at the same time as samples and is taken through the entire sample analysis process. It is used to monitor the laboratory preparation and analysis systems for interferences

and contamination from glassware, reagents, sample manipulations, and the general laboratory environment.

4.2.2. SOLVENT BLANK – An aliquot of solvent analyzed with each batch of samples to indicate any contamination or artifacts that may come from the reagents and analytical steps.

4.2.3. FIELD BLANK – An XAD-2 resin tube that goes out to the field and is treated as a sample where it will be connected to a sampler, disconnected without pulling an air sample, and returned to the laboratory. Field blanks are treated like samples in the laboratory. The field blank identifies any potential contamination that may occur from ambient conditions, sample handling, or other sources that samples may be exposed to.

4.3. BREAKTHROUGH – Breakthrough analysis refers to analyzing the secondary sorbent bed of the XAD-2 resin tube to determine if any amount of sample was not retained in the primary sorbent bed.

4.4. BREAKTHROUGH THRESHOLD LIMIT – The concentration found in the primary sorbent bed that would require analysis of the secondary sorbent bed.

4.5. CALIBRATION CURVE – The calibration curve is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration.

4.6. CARRYOVER – Contamination from an adjacent sample causing false or inaccurate results in the subsequent sample(s).

4.7. COLLOCATED SAMPLE – A sample used to assess total precision (sampling and analysis) which is located within a specified radius of the primary sampler. The collocated sampler must be identical in configuration and operation to the primary sampler. The collocated sample is processed identically to the primary sample.

4.8. CONTINUING CALIBRATION VERIFICATION – A midpoint calibration standard analyzed, at a minimum, once per every ten samples and at the end of the analytical batch to confirm the stability of the instrument calibration.

4.9. CONTROL STANDARD – A midpoint standard which is analyzed after the calibration curve. The control standard should be prepared with stock standards that are different from those used to prepare the calibration

standards, when available. The control standard should be prepared by a second analyst if a second stock is not available. The control standard must be analyzed at a minimum of once per batch.

4.10. DILUTIONS – Dilution is the process of reducing the concentration of a solute in solution, usually by adding more solvent. Dilutions are required when any sample concentration exceeds the calibrated linear range by more than ten percent. After diluting, the concentration should fall within the calibrated linear range. Additional dilutions are sometimes necessary.

4.11. ESTIMATED QUANTITATION LIMIT – The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL may be used as the reporting limit for special projects, if requested.

4.12. HOLD TIME – The maximum amount of time a sample or extract may be stored prior to performing an operation. Extraction hold time is from sample collection to extracting the sample. Analytical hold time is from sample extraction to analysis.

4.13. INTERFERENCE – Discrete artifacts or elevated baselines from solvents, reagents, glassware, and other sample processing hardware that may cause misinterpretation of the chromatographic data. Other interferences are matrix effects which may cause the target compound to recover higher or lower than the expected value.

4.14. METHOD DETECTION LIMIT – A statistically derived value that is defined as being the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix (including sample media) containing the analyte. The procedure used to determine the MDL is documented in the NLB's Laboratory QCM.

4.15. REPLICATE – A second analysis of a randomly chosen sample within an analytical batch.

4.16. REPORTING LIMIT – Equivalent to the lowest level of the calibration curve. Detections below the reporting limit are typically reported as "<RL" unless otherwise requested by the client.

4.17. SPIKE – A known concentration of a standard containing target analytes is added to sampling media or reagent. Spike recoveries indicate efficiency of laboratory and/or field procedures.

4.17.1. FIELD SPIKE – An XAD-2 resin tube spiked with a known concentration of target analyte that goes out to the field and is treated as a sample, where it will be connected to a sampler and sampled as normal to check for matrix effects.

4.17.2. LABORATORY CONTROL SPIKE – A laboratory control spike is an XAD-2 resin tube spiked with a known concentration that is prepared, extracted, and analyzed with every batch of samples. LCS recoveries indicate extraction efficiency.

4.17.3. TRIP SPIKE – An XAD-2 resin tube is spiked with a known concentration of target analyte, shipped along with sampling media, and is taken into the field, but returned unopened to the laboratory. Trip spike recoveries indicate if samples may have been affected by shipping conditions.

5. Interferences and Limitations

5.1. Interferences may be caused by contaminants in the filters, sampling media, solvents, sample extraction apparatus, filtration apparatus, and glassware. A method blank is extracted and analyzed with each set of samples to monitor these possible sources of contamination.

5.2. A LCS is prepared by the addition of a known amount of target analyte onto an XAD-2 resin tube followed by the same extraction, filtration, and analytical processes as performed on the samples. LCS recoveries indicate potential background interferences inherent in the resin which may cause lower or higher recoveries of target compounds.

5.3. Analysis of an analytical batch should begin immediately following extraction. If extracts cannot be analyzed on the day of extraction, the extracts are placed in a freezer until analysis is possible, ensuring not to exceed analytical hold time of one month.

5.4. The analytical system may become contaminated when samples containing high compound concentrations are analyzed. If there is suspected carryover from a high concentration sample, additional blanks should be analyzed to clean the system prior to reanalyzing the succeeding sample(s) to verify results.

5.5. High boiling point compounds trapped on the column may cause baseline shifting, or the appearance of broad, extraneous “ghost” peaks. The column should be baked out to remove these contaminants prior to

analyzing samples. The bake out temperature must not exceed the column's maximum operating temperature.

6. Personnel Qualifications and Training

Prior to performing this method, new personnel must be trained by staff with expert knowledge of this method. Personnel must be trained to understand the program's requirements per any applicable State and federal regulations and guidance, and this SOP. Personnel will also be trained on how to safely and properly operate the equipment needed to perform the method, the quality assurance components, waste disposal, and LIMS functionality pertaining to the program. Personnel should provide an initial demonstration of capability prior to performing this method on real-world samples (i.e. data for record). Training will be documented and maintained by the laboratory supervisor.

7. Safety Requirements

All personnel must follow the general health and safety requirements found in NLB's Chemical Hygiene Plans.

Organophosphates are cholinesterase inhibitors. Direct contact with the skin can cause ciliary muscle spasms and blurred vision. The analyst should refer to the SDS of all pesticides included in this method for additional information regarding chemical properties and precautions.

The handling and preparation of samples, extracts, and standards must be conducted in a hood. Proper personal protective equipment must be worn, including neoprene or nitrile gloves, safety glasses, and a laboratory safety coat. Analysts should ensure that engineering and air quality controls are active and operating properly to reduce or eliminate off-gassing from instrument exhaust ports.

This method uses high pressure gases. Refer to safe handling practices in the Chemical Hygiene Plan regarding compressed gases when moving and installing the cylinders.

The GC and MS have heated zones which may cause burns. Avoid contact with these zones and devices when in operation and make certain they are at ambient temperature prior to servicing.

8. Hazardous Waste

Organophosphate waste is categorized as toxic. Some of the pesticides are categorized as acutely toxic, and therefore, the waste must be disposed of within

90 days upon accumulation of 1.0 kg. The NLB Health and Safety Coordinator (H&SC) should be notified upon accumulation of 1.0 kg (approximately two pounds) of this waste. Waste consists of the sample vials containing organophosphate pesticides and glass sampling tubes which should be stored in the small two gallon waste buckets under the hood which serve as the satellite accumulation area. The buckets should be properly labeled with appropriate hazardous waste labels which indicate the contents and start date of accumulation. When a bucket becomes full, or when 1.0 kg has accumulated, notify the NLB H&SC and move the full bucket to the main hazardous waste storage area. The NLB H&SC will provide a new bucket for the satellite collection area.

9. Equipment and Supplies

9.1. Gas Chromatograph: system with programmable oven, electronic pressure control for capillary columns with safety feature shutdown when gas pressures falls below set levels, programmable heated injector, and automated liquid injector

9.2. Column: Thermo TG-5 SilMS, 30 meter, 0.25 mm inner diameter, 0.25 µm film thickness, or equivalent

9.3. Detector: MS/MS

9.4. Syringe Filters: Disposable PTFE 0.2 µm Filter (13 mm -25 mm GD/X)

9.5. Disposable Syringes: 3 mL volume such as BD disposable syringes part# 309656

9.6. 4 mL glass storage vials with Teflon lined screw caps

9.7. Ultrasonic bath: capable of temperature programing such as Branson model 8510

9.8. 8 mL glass extraction vials

9.9. Autosampler deactivated vials with cap

9.10. Autosampler 250 µL flat bottom inserts

9.11. Volumetric Flasks: 5 mL, 10 mL, 25 mL, 50 mL, and 100 mL volume ranges

9.12. XAD-2 resin tubes: 400/200 (mg) such as SKC catalog # 226-30-06

9.13. Analytical balance capable of weighing as low as 0.1 mg

9.14. Eppendorf electronic pipettes: 15 - 5000 µL volume ranges

9.15. 1.5 mL disposable Pasteur pipettes

9.16. Tweezers

9.17. Hand-held glass cutter

9.18. Disposable nitrile or neoprene gloves to handle organic solvents

9.19. Hamilton microliter syringes (or equivalent): 10 µL, 25 µL, 250 µL, 500 µL, and 1000 µL volume ranges

10. Reagents and Gases

10.1. Pesticide residue grade ethyl acetate or better, CAS No 141-78-6, such as Burdick & Jackson

10.2. Helium Ultra-High Purity (UHP), 99.999 percent for use as the GC column carrier gas

10.3. Argon Ultra-High Purity (UHP), 99.999 percent for use as the collision gas

11. Standards Preparation

All standard solutions are stored in a freezer until used. The standard solutions are removed from the freezer and allowed to equilibrate to room temperature before use. Standards should be returned to the freezer at the end of the work day. Neat standards are valid up to the manufacturer's expiration date. Working standards expire one year from preparation date, but are not to exceed the expiration date of the neat or parent solution. The pesticides analyzed by this method are listed below:

Chlorpyrifos	CAS Number	2921-88-2
Chlorpyrifos OA	CAS Number	5598-15-2
DEF	CAS Number	78-48-8
Diazinon	CAS Number	333-41-5
Diazinon OA	CAS Number	962-58-3
Dichlorvos	CAS Number	62-73-7
Dimethoate	CAS Number	60-51-5
Dimethoate OA	CAS Number	1113-02-6
Malathion	CAS Number	121-75-5
Malathion OA	CAS Number	1634-78-2
Phosmet	CAS Number	732-11-6

11.1. Standard Preparations

11.1.1. Individual stock standards (1.0 – 5.0 mg/mL) are prepared by separately weighing out 0.025 – 0.050 grams neat of each

organophosphate pesticide in a 10 - 25 mL volumetric flask and filling to volume with pesticide residue grade or better of ethyl acetate.

Calculate the concentration of the individual stock standards using the following formula:

$$Stock\ standard\ concentration = weight\ of\ neat\ (g) / size\ of\ volumetric\ flask\ (mL)\ x\ 1000\ mg/g$$

For example, if a weight of 0.0391g was recorded, using a 25 mL volumetric flask:

$$Stock\ standard = 0.0391 g/25 mL\ x\ 1000\ mg/g = 1.564\ mg/mL$$

11.1.2. A mixed standard solution of 100 µg/mL is made by adding aliquots of each stock solution to a 10 mL volumetric flask and filling to volume with residue grade or better ethyl acetate.

The calculation to determine the volume of each aliquot is as follows (using an example stock standard at 1.564 mg/mL):

$$Aliquot = \frac{100\ \mu g/mL \times 10\ mL}{1.564\ mg/mL \times 1000\ \mu g/mg \times 1mL/1000\ uL} = 640\ \mu L$$

Using this example to make a 100 µg/mL standard, the analyst would take 640 µL of the 1.564 mg/mL stock and dilute to 10 mL.

For the lower calibration levels, a mixed standard solution of 10 µg/mL is prepared by making a 1:10 dilution of the 100 µg/mL mixed standard solution.

11.1.3. Each working calibration standard is prepared by spiking the mixed standard solution described in 11.1.2 onto the primary sorbent bed of an XAD-2 tube, which is then extracted with 4mL of ethyl acetate. Only the spiked primary sorbent bed is extracted, as breakthrough is not expected. Typical calibration levels are prepared as shown in Table 1. Working calibration

standards may be used for four weeks after preparation, or until degradation is observed (i.e. recoveries start to drift outside expected results).

Table 1. Typical Calibration Levels

Calibration Level	Std. Conc. (µg/mL)	Spiking Vol (µL)	Extraction Vol (µL)	Final Conc. (µg/mL)
Level 1	10	4.0	4.0	0.01
Level 2	10	20.0	4.0	0.05
Level 3	10	40.0	4.0	0.1
Level 4	100	20.0	4.0	0.5
Level 5	100	40.0	4.0	1.0

11.2. LCS and Control Standards

11.2.1. A 0.4 µg/mL LCS is prepared by spiking 16 µL of the 100 µg/mL spiking solution onto an XAD-2 resin tube and extracted with 4 mL of ethyl acetate. One LCS is to be extracted and analyzed with every batch.

11.2.2. The control standard stocks and mix are prepared as described in sections 11.1.1 and 11.1.2. The control standard should be prepared from a different lot of neat standards than what was used for the calibration standards, when available. A working control standard is prepared by spiking 10 µL of the 100 µg/mL control mix onto an XAD-2 tube and extracting with 4mL of ethyl acetate for a final concentration of 0.25 µg/mL.

11.3. Field Spikes and Trip Spikes

11.3.1. Prepare a 100 µg/mL spiking solution (see section 11.1).

11.3.2. A spiked 0.4 µg/mL field spike is prepared by spiking 16 µL of the 100 µg/mL spiking solution onto an XAD-2 resin tube. A trip spike is prepared in the same manner as a field spike. The spiked tube is labeled with the date and time, along with the designation “field spike” or “trip spike”. The tube is then secured in a screw top glass storage tube and stored in a freezer.

12. Media and Sample Storage

12.1. Media storage – Prior to sampling, sorbent tubes are stored and shipped at ambient temperature. Once the tubes are spiked or sampled, Field Sample Storage conditions apply.

12.2. Field Sample Storage – The field operator will place the collected samples/QC in individual screw top glass storage tubes. The tubes are stored in a cooler with blue ice or dry ice at 5°C or less until returned to the laboratory. Temperature indicator strips which indicate below 5ºC and above 25ºC are packed with the samples. The receipt temperature (either below 5ºC, between 5ºC and 25ºC, or above 25ºC) is included with reported sample results.

12.3. Laboratory Sample Storage – The samples/QC are stored in a freezer until extraction.

13. Sample Extraction and Analysis

13.1. Sample Preparation and Extraction

13.1.1. Samples collected on XAD-2 resin tubes are stored in a freezer until extraction. Prior to sample analysis, remove the samples from the freezer and allow them to equilibrate at room temperature. All samples must be extracted within one month of the sampling date.

13.1.2. Obtain the necessary amount of 8 mL glass vials (one for each XAD-2 resin tube) and put them on a sampling tray. Label each one clearly with their sample IDs and extraction dates. A LCS and method blank must be prepared with each batch of samples.

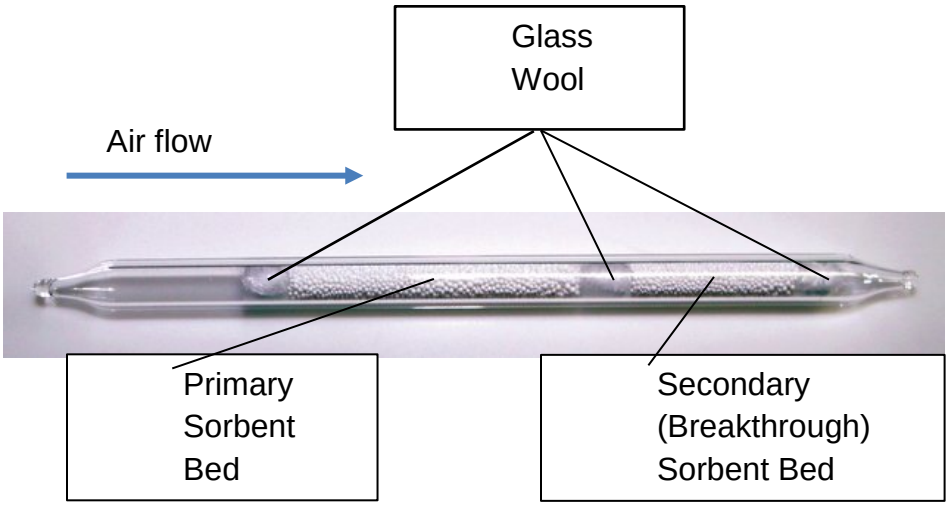
13.1.3. The XAD-2 resin tube is comprised of two sections separated by glass wool, a longer end (primary sorbent bed) used for sample analysis and a shorter end (secondary sorbent bed) used to test for sample breakthrough. One breakthrough (secondary sorbent bed) analysis should be done for every 10 samples, at a minimum.

Breakthrough studies have demonstrated no breakthrough for samples with up to 1.0 µg/mL of target analytes spiked onto the primary sorbent bed (see Table 8). If target analytes over 1.0 µg/mL are detected in any sample's primary sorbent bed,

analysis of the secondary sorbent bed must be done to check for breakthrough.

A new breakthrough threshold limit may be established if analyte detections in the primary sorbent bed consistently exceeds the breakthrough threshold limit's specified concentration. A series of spiked primary sorbent beds, along with the respective secondary sorbent beds, are analyzed. Alternately, a series of high concentration samples, along with their respective secondary sorbent beds, may be analyzed. The breakthrough threshold limit is the concentration of the highest primary sorbent bed. There must be a pattern of no target analyte concentration found in the secondary sorbent bed for a breakthrough threshold limit to be determined.

13.1.4. Carefully remove the XAD-2 resin tube from the glass storage tube and remove the red cap from the end of the primary sorbent bed. Remove the glass wool plug using tweezers. If any of the glass wool contains XAD-2 resin, shake off the XAD-2 resin into the 8 mL vial. If you are not able to shake off all the XAD-2 resin, the glass wool can be added to the 8 mL vial for extraction.



13.1.5. After removing the front glass wool, pour the XAD-2 resin from the primary sorbent bed into 8 mL glass vial.

13.1.6. Score the tube with the glass cutter just in front of the second section of glass wool and carefully break the tube. Empty any remaining resin left in the primary sorbent bed into the 8 mL vial. Using an automatic pipette, rinse the empty primary sorbent bed

of the cut-off tube with 4 mL of ethyl acetate, collecting the solvent in the 8 mL glass vial. Cap the vial securely.

13.1.7. If breakthrough analysis is being done, extract the secondary sorbent bed as described in 13.1.6 as a separate sample. Shake off any resin remaining in the glass wool into the 8 mL vial. If you are not able to shake off all the XAD-2 resin, the glass wool can be added to the 8 mL vial for extraction.

13.1.8. Prepare a method blank with every extraction batch by opening an unused, clean XAD-2 resin tube.

13.1.9. Prepare a LCS with every extraction batch by opening an unused, clean XAD-2 resin tube and spiking the resin tube with 16 µL of the 100 µg/mL spiking solution onto the primary sorbent bed.

13.1.10. Repeat steps 13.1.4 through 13.1.7 for the LCS, method blank, field spike, trip blank, trip spike, and all samples scheduled for analysis.

13.1.11. Place all vials containing extracts in an ultrasonic bath for one hour at room temperature.

13.1.12. After sonication, remove the vials of extracts from the sonication water bath. Filter each extract into individual 4 mL glass vials using a 3 mL disposable syringe and a disposable 0.20 µm PTFE syringe filter. Label each one clearly with their sample ID and extraction date.

13.1.13. Transfer approximately 250 µL of each extract into individual 1.5 mL autosampler vials equipped with a 250 µL insert.

13.1.14. Randomly choose one sample extract as a replicate to be analyzed a second time. One replicate must be analyzed for every 10 samples, at a minimum.

13.1.15. Transfer approximately 250 µL of the working calibration standards and control standard into individual 1.5 mL autosampler vials equipped with a 250 µL insert. The extracts and standards are now ready for analysis. If extracts cannot be analyzed on the day of extraction, place the extracts in a freezer.

13.1.16. All extracted samples must be analyzed within one month from extraction.

13.2. Sample Analysis

13.2.1. Analytical Sequence

Each analytical batch of 10 or fewer samples must include bracketing standards, controls, replicates, and blanks as listed below. A 0.7 µL injection volume is used for all analyses. The recommended order of analysis is as follows:

- Solvent blank
- Calibration standards
- Control standard
- Solvent blank
- Laboratory Control Spike
- Method Blank
- Samples (up to 10 including breakthrough analyses)
- Breakthrough analysis (one every 10 or fewer samples)
- Replicate (one every 10 or fewer samples)
- Solvent blank
- CCV standard

13.2.2. GC-MS/MS Analytical Conditions

GC:

- Thermo Fisher Scientific GC Trace 1310
- Liner: Baffled PVT 2mm x 2.75mm x 120mm
- Injector: 275 °C
- Flow mode: Constant flow
- Split Mode: CT splitless
- Column: Thermo TG-5 SilMS, 30 meter, 0.25 mm inner diameter, 0.25 µm film thickness
- GC Temperature Program: Oven initial 55 °C, hold 4 min, Ramp to 200 °C at 10 ˚C/min, ramp to 260 °C at 20 °C /min
- Total run time 22.5 minutes
- Splitter open at 1 min
- Carrier Gas: UHP Helium
- Column Flow: Helium, 1.5 mL/min, 93.5 kPa
- Splitter: 10 mL/min

MS/MS:

- Ionization Mode: Electron Ionization Positive Mode
- Collision Gas: UHP Argon
- Acquisition Mode: Selective Reactive Monitoring
- Tuning: PFTBA on masses 69, 131, 219, 414, 502
- Transfer line temperature 250 °C

Run parameters and MS quantitation ions for each compound are listed in Table 2 and Table 3.

Table 2. MS/MS Run Parameters

Compound	Retention Time (min)	Scan Window (min)	Precursor Mass (m/z)	Product Mass (m/z)	Collision Energy (eV)
Dichlorvos	9.01 9.01	0.5 0.5	109 185	79 93.1	5 10
Dimethoate OA	11.42 11.42 11.42	1.5 1.5 1.5	156.1 156.1 156.1	79.1 80.1 110.1	20 15 10
Dimethoate	12.35 12.35 12.35	1.25 1.25 1.25	87 93 125	42.1 63.1 79.1	10 10 10
Diazinon OA	12.53 12.53 12.53	0.5 0.5 0.5	137.1 217.1 273.2	84.1 119.1 137.2	10 10 10
Diazinon	12.72 12.72	0.5 0.5	137.1 152.2	84.1 137.2	10 10
Malathion OA	13.39 13.39 13.39	0.5 0.5 0.5	99.1 127.1 127.1	71.1 99.1 109.1	10 5 10
Malathion	13.94 13.94	0.5 0.5	127.1 173.1	99.1 99.1	5 15
Chlorpyrifos OA	13.97 13.97 13.97	0.5 0.5 0.5	197 242 270	169 150 242	10 20 10
Chlorpyrifos	14.08 14.08 14.08	0.5 0.5 0.5	257.9 257.9 314.1	166 194 258	20 15 15
DEF	15.67 15.67 15.67	0.5 0.5 0.5	147 169.1 202	113 57.1 147	10 10 5
Phosmet	17.78 17.78	0.5 0.5	160.1 160.1	77.1 133.1	20 10

Table 3. MS/MS Quantitation Ions

Compound	Quantitation Ion
Dichlorovos	93.1
Dimethoate OA	110.10
Dimethoate	42.10
Diazinon OA	84.10
Diazinon	84.10
Malathion OA	71.00
Malathion	99.10
Chlorpyrifos OA	242.00
Chlorpyrifos	166.00
DEF	147.00
Phosmet	77.10

Instrument tuning is done using the software parameters detailed on the Dashboard screen. Table 4 shows a list of tunes available for this analysis and recommended frequency. Tuning is done prior to the analytical sequence.

Table 4. MS/MS Tuning Guide

Tune Type	Tune Description	Recommended
EI Diagnostics Only	Runs complete diagnostics and generates report. No tuning is performed. Starts with last saved tune.	Used to check and troubleshoot MS
EI SRM Tune	Complete EI Tuning. Q3 MS tuning. More sensitive for high mass than EI Standard tune by tuning resolution at 50% peak height. Sets mass 219 to 20 million counts. Starts with last saved tune.	6 to 12 months or earlier if needed
EI SRM Quick Tune	Q3 MS tuning. More sensitive for high mass than EI Standard tune by tuning resolution at 50% peak height. Sets mass 219 to 20 million counts. Starts with last saved tune.	3 to 6 months
EI Target Tune	Adjust ion ratios of calibration gas for a typical quadrupole spectra. Starts with last saved tune. Sets mass 219 to 20 million counts.	1 to 6 months
EI Tune Check	Generates a report after setting mass 219 to 20 million counts and performing a leak check. Starts with last saved tune.	Daily

14. Quality Control

Several types of samples are analyzed to ensure and assess the quality of the data. These samples, acceptance criteria, and corrective actions are described in Table 5. If QC results do not meet criteria, corrective action must be taken. All anomalies, corrective actions, and deviations from this SOP must be documented in the chemist's logbook, monthly QC report, and in the final data report.

Table 5. Quality Control Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
Sample Hold Time (prior to extraction)	All samples	Store samples in freezer until extraction. Extract within one month from collection date.	If hold time is exceeded, document and report.
Analytical Hold Time	All sample extracts	Store extracts in freezer until analysis. Analyze within one month from extraction.	If hold time is exceeded, document and report.
Method Blank	One per extraction batch at a minimum	<RL	If > RL check instrument and method materials for possible contamination, reanalyze method blank and all samples in batch. Evaluate sample results; when sample results are less than ten times higher than method blank results, results are invalidated for those samples associated with the blank.
Solvent Blank	One per analytical batch at a minimum	<RL	If > RL check instrument and solvent materials for possible contamination, reanalyze solvent blank and all samples in batch.
Field Blank	Per client request or field protocol	<RL	If > RL reanalyze to confirm results. Investigate if still outside criteria. Report results if no analytical issues are found.

Table 5. Quality Control Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
Breakthrough	One per ten samples at a minimum; samples with > 1.0 µg/mL analytes in primary sorbent bed	No target analytes detected above RL in secondary sorbent bed	If analytes were found above RL in secondary sorbent bed, reanalyze secondary sorbent bed to confirm breakthrough. Evaluate other samples in the analytical batch and determine threshold limits; extract and analyze secondary sorbent beds of any samples that had detections over the threshold limit in the primary sorbent bed.
Initial Calibration	Five calibration levels prior to analysis	$R^2 \geq 0.98$	Reanalyze. Prepare new calibration standards if criteria still not met.
Carryover Check	After analysis of high concentration sample	No target analytes detected above top of linear range	Reanalyze subsequent sample(s) to confirm results are not biased high due to contamination from analysis of preceding high concentration sample. If reanalysis results meet replicate criteria, report results. If not, analyze blanks to clean system. Reanalyze samples once system is clean.
Collocated Samples	Per client request (typically 10% of field samples) or field protocol	RPD ±25%	Verify results by reviewing data. Report results. Notify client if outside criteria.
Continuing Calibration Verification (CCV)	A midpoint calibration standard analyzed after ten or fewer samples and at end of analytical batch	Ending and bracketing CCV must be ±30% of the expected value.	Reanalyze CCV that failed and all preceding samples that are not bracketed by CCV that met criteria. Prepare new CCV if criteria still not met. Reanalyze all samples with new CCV.

Table 5. Quality Control Corrective Actions

QC Type	Frequency	Criteria	Corrective Action
Control Standard (CS)	After calibration and before sample analysis	One CS must be analyzed with every analytical batch. CS must fall within established control criteria as described in QCM.	Reanalyze CS. Prepare new CS if criteria still not met. Reanalyze all samples with new CS.
Replicate	One per ten or fewer samples in analytical batch at a minimum	RPD ±25%	Reanalyze replicate and all associated samples within bracketing standards. If still outside criteria, investigate and correct issues. Reanalyze. Invalidate all samples in batch if replicate fails again.
Laboratory Control Spike (LCS)	One per extraction batch	70-130% of expected value	Reanalyze LCS and all associated samples in the batch. If the LCS still does not meet criteria, and all other QC passes, further investigation is required.
Field Spike	Per client request or field protocol	70-130% of expected value	Reanalyze to confirm results. Investigate if still outside criteria. Report results if no analytical issues are found.
Trip Spike	Per client request or field protocol	70-130% of expected value	Reanalyze to confirm results. Investigate if still outside criteria. Report results if no analytical issues are found.

15. Calculations

15.1. Relative Percent Difference (RPD) between two results is calculated as follows:

$$RPD = \frac{|X1 - X2|}{(X1 + X2)/2} \; x \; 100\%$$

Where:
X1 = first measurement value
X2 = second measurement value

15.2. Field spike percent recoveries are calculated as:

$$\left(\frac{(Field\ spike\ concentration - \text{primary}\ sample\ concentration)}{Spiked\ Amount}\right) \text{x}100\%$$

15.3. Laboratory Control Sample percent recoveries are calculated as follows:

$$\left(\frac{LCS\ Concentration}{Spiked\ Amount}\right) \times 100\%$$

15.4. Trip Spike percent recoveries are calculated as:

$$\left(\frac{Trip\ Spike\ Concentration}{Spiked\ Amount}\right) \times 100\%$$

15.5. Standard Preparation Calculations (see section 11.1)

15.5.1. Stock Standard mg/mL concentration is calculated as follows:

$$Stock\ standard\ concentration = weight\ of\ neat\ (g) / size\ of\ volumetric\ flask\ (mL)\ x\ 1000\ mg/g$$

15.5.2. Aliquot volumes for the mixed standard solution at 100 µg/mL are calculated as follows:

$$Aliquot\ (\mu L) = \frac{{}^{100\mu g}/_{mL}\ x10mL}{stock({}^{mg}/_{mL})x\ {}^{1000\mu g}/_{mg}\ x\ {}^{1mL}/_{1000\mu L}}$$

15.6. Final reporting limits of µg/sample are calculated using the 4 mL extraction volume as follows:

$${}^{4mL}/_{sample}\ x\ (\mu g/mL\ sample\ conc\ x\ dilution\ factor) = sample\ conc\ (\mu g/sample)$$

16. Data Management and Reporting

Data management consists of samples logged into LIMS, documentation of unusual occurrences and their resolutions, creation of data packages (monthly, amendments, and special projects) for peer review and management approval, submittal of data to clients, and archival procedures for sample media and respective chains of custody. Program and maintenance notebooks and/or logbooks are to be kept with the instrumentation at all times.

16.1. After data acquisition, the raw data files are processed by the analytical software to produce result files. The result files contain quantitation information such as peak areas and retention times, along with concentration and instrumentation information.

16.2. Peaks found in the chromatogram are verified by the chemist that they were identified correctly. Integration of each peak is evaluated to ensure the software processed the data appropriately.

16.3. The instrument method is calibrated for both retention time and concentration during data processing using the integrated calibration standard areas. The concentrations of target compounds are based on the peak areas and the known analyte concentrations in the standards. Concentrations are calculated using the instrument standardization routine for samples, blanks, controls, and spikes. Retention times are verified that the peaks are not shifting more than ± 0.10 minutes. If shifting occurs, maintenance may need to be performed and samples reanalyzed.

16.4. The final results will be adjusted by an appropriate dilution factor (only if the sample was diluted; otherwise, the dilution factor would be 1.00) and reported in µg/sample.

16.5. All QC and sample results are verified by the chemist and then sent to LIMS for archive and reporting. Data is reviewed by a peer chemist and management before being released.

16.6. Analyte concentrations will not be reported if below the RL unless otherwise requested by the client. (i.e., client requires 5x MDL be reported as “EQL” and concentrations between the MDL and EQL be reported as “Trace”.)

17. Maintenance and Repairs

Preventive maintenance is done on an annual basis on the GC-MS/MS and repairs are done as needed by an approved vendor under contract to MLD or by experienced staff. All maintenance and repairs are documented in a logbook. Injection port septa should be replaced after approximately 200 injections.

18. Method Development

Stability studies were conducted on working standards and laboratory spikes over a four week period. Laboratory spikes were made at 0.025 µg/mL and 1.0 µg/mL and analyzed after being held for three and four weeks. A working

standard at 0.05 µg/mL was analyzed once per week for four weeks. All standards and spikes were found to be stable over the four week time frame.

Tables 6 – 9 below summarize method development studies including the initial MDL determination, initial control limits, breakthrough studies, and stability studies.

Table 6. Initial MDL Determination

		Dichlorovos	Dimethoate OA	Dimethoate	Diazinon OA	Diazinon	Malathion OA
Replicate	Conc. (µg/mL)	µg/mL	µg/mL	µg/mL	µg/mL	µg/mL	µg/mL
1	0.010	0.0118	0.0125	0.0119	0.0109	0.0110	0.0138
2	0.010	0.0113	0.0120	0.0104	0.0103	0.0108	0.0113
3	0.010	0.0119	0.0129	0.0103	0.0110	0.0115	0.0126
4	0.010	0.0120	0.0121	0.0117	0.0106	0.0113	0.0126
5	0.010	0.0121	0.0126	0.0105	0.0107	0.0112	0.0133
6	0.010	0.0122	0.0126	0.0107	0.0103	0.0111	0.0121
7	0.010	0.0114	0.0118	0.0102	0.0099	0.0109	0.0117
8	0.010	0.0117	0.0130	0.0114	0.0106	0.0116	0.0122
Average		0.012	0.012	0.011	0.011	0.011	0.012
Median		0.012	0.013	0.011	0.011	0.011	0.013
Std.Dev. (σ)		0.0003	0.0004	0.0007	0.0004	0.0002	0.0009
$t_{01,2}$ =	2.998						
MDL	$t_{01,2}$ * σ	0.0010	0.0013	0.0020	0.0011	0.0008	0.0024
EQL	5*MDL	0.005	0.006	0.010	0.005	0.004	0.012
Method RL (µg/mL)		0.010	0.010	0.010	0.010	0.010	0.010

Table 6. Initial MDL Determination

Replicate	Conc. (µg/mL)	Malathion µg/mL	Chlorpyrifos OA µg/mL	Chlorpyrifos µg/mL	DEF µg/mL	Phosmet µg/mL
1	0.010	0.0110	0.0116	0.0121	0.0106	0.0118
2	0.010	0.0106	0.0112	0.0120	0.0099	0.0113
3	0.010	0.0114	0.0122	0.0128	0.0114	0.0116
4	0.010	0.0110	0.0119	0.0121	0.0111	0.0118
5	0.010	0.0109	0.0112	0.0122	0.0102	0.0114
6	0.010	0.0108	0.0127	0.0126	0.0098	0.0113
7	0.010	0.0104	0.0117	0.0122	0.0101	0.0110
8	0.010	0.0107	0.0117	0.0130	0.0104	0.0110
Average		0.011	0.012	0.012	0.010	0.011
Median		0.011	0.012	0.012	0.010	0.011
Std.Dev. (σ)		0.0003	0.0005	0.0003	0.0006	0.0003
$t_{01,2}$ =	2.998					
MDL	$t_{01,2}$ * σ	0.0009	0.0015	0.0011	0.0017	0.0009
EQL	5*MDL	0.005	0.008	0.006	0.009	0.005
Method RL (µg/mL)		0.010	0.010	0.010	0.010	0.010

MDL verifications are performed annually, at a minimum, per the QCM. MDL values are subject to change based on the verification results.

Table 7. Initial Control Limits

Compound	Dichlorovos	Dimethoate OA	Dimethoate	Diazinon OA	Diazinon	Malathion OA
Expected Conc. (µg/mL)	0.25	0.25	0.25	0.25	0.25	0.25
Number of Control Samples	25	25	25	25	25	25
Average	0.328	0.261	0.304	0.296	0.258	0.277
Median	0.327	0.256	0.301	0.299	0.256	0.283
sd	0.018	0.018	0.017	0.025	0.018	0.022
%RSD	5.53%	6.93%	5.44%	8.31%	7.07%	7.91%
UCL	0.382	0.315	0.353	0.37	0.312	0.343
UWL	0.364	0.297	0.337	0.345	0.294	0.321
LWL	0.291	0.224	0.271	0.247	0.221	0.233
LCL	0.273	0.206	0.254	0.222	0.203	0.211

Compound	Malathion	Chlorpyrifos OA	Chlorpyrifos	DEF	Phosmet
Expected Conc. (µg/mL)	0.25	0.25	0.25	0.25	0.25
Number of Control Samples	25	25	25	25	25
Average	0.283	0.270	0.247	0.269	0.267
Median	0.282	0.266	0.246	0.269	0.272
sd	0.023	0.016	0.013	0.018	0.023
%RSD	8.25%	6.00%	5.24%	6.63%	8.76%
UCL	0.354	0.318	0.285	0.323	0.337
UWL	0.330	0.302	0.272	0.305	0.314
LWL	0.237	0.237	0.221	0.233	0.220
LCL	0.213	0.221	0.208	0.216	0.197

Table 8. XAD-2 Breakthrough Study

Compound	Primary Sorbent Bed Breakthrough Spike Level (µg/mL)							
	0.01	0.10	0.25	0.25	0.50	1.0	1.0	1.0
Dichlorvos	0.0114	0.1007	0.2706	0.2708	0.5036	1.0185	1.0268	0.9721
Dimethoate OA	0.0157	0.1119	0.3218	0.3114	0.5701	1.0574	1.0943	1.0049
Dimethoate	0.0122	0.1106	0.2918	0.2786	0.5199	1.0365	1.0372	0.9765
Diazinon OA	0.0123	0.1081	0.2774	0.2782	0.5010	1.0690	1.0632	0.9944
Diazinon	0.0121	0.1016	0.2791	0.2768	0.5074	1.0484	1.0376	0.9939
Malathion OA	0.0143	0.1101	0.2945	0.2910	0.5150	1.0559	1.0708	0.9957
Malathion	0.0115	0.1061	0.2799	0.2735	0.5019	1.0663	1.0570	0.9879
Chlorpyrifos OA	0.0126	0.1161	0.2945	0.2818	0.5288	1.0779	1.0928	1.0191
Chlorpyrifos	0.0130	0.1020	0.2836	0.2749	0.5213	1.0368	1.0379	1.0027
DEF	0.0103	0.1130	0.2756	0.2602	0.4866	1.0608	1.0790	0.9724
Phosmet	0.0128	0.1133	0.2846	0.2651	0.4957	1.0715	1.1160	1.0047

The secondary sorbent bed was analyzed for all spikes in this study. No breakthrough was detected.

Table 9. Matrix Stability Study

Week 3 Matrix Stability Study				
Compound	0.025 µg/mL spike	1.0 µg/mL spike	% Recovery at 0.025 µg/mL	% Recovery at 1.0 µg/mL
Dichlorvos	0.0293	1.0758	117	108
Dimethoate OA	0.0284	1.1035	114	110
Dimethoate	0.0277	1.0864	111	109
Diazinon OA	0.0268	1.0896	107	109
Diazinon	0.0259	1.0720	104	107
Malathion OA	0.0249	1.1006	100	110
Malathion	0.0260	1.0997	104	110
Chlorpyrifos OA	0.0283	1.1328	113	113
Chlorpyrifos	0.0252	1.0722	101	107
DEF	0.0278	1.1404	111	114
Phosmet	0.0288	1.1078	115	111

Week 4 Matrix Stability Study				
Compound	0.025 µg/mL spike	1.0 µg/mL spike	% Recovery at 0.025 µg/mL	% Recovery at 1.0 µg/mL
Dichlorvos	0.0287	1.0252	115	103
Dimethoate OA	0.0281	0.9821	112	98
Dimethoate	0.0273	1.0084	109	101
Diazinon OA	0.0284	1.0068	114	101
Diazinon	0.0266	1.0153	106	102
Malathion OA	0.0268	0.9877	107	99
Malathion	0.0277	1.0189	111	102
Chlorpyrifos OA	0.0280	1.0462	112	105
Chlorpyrifos	0.0265	1.0237	106	102
DEF	0.0292	1.0162	117	102
Phosmet	0.0269	1.0122	108	101

Table 10. Working Standard Stability Study

Compound	Week 1 0.05 µg/mL	Week 2 0.05 µg/mL	Week 1 % Recovery	Week 2 % Recovery
Dichlorvos	0.0538	0.0458	108	92
Dimethoate OA	0.0498	0.0472	100	94
Dimethoate	0.0488	0.0440	98	88
Diazinon OA	0.0536	0.0456	107	91
Diazinon	0.0533	0.0425	107	85
Malathion OA	0.0556	0.0477	111	95
Malathion	0.0538	0.0468	108	94
Chlorpyrifos OA	0.0522	0.0457	104	92
Chlorpyrifos	0.0549	0.0405	110	81
DEF	0.0561	0.0455	112	91
Phosmet	0.0542	0.0453	108	91

Compound	Week 3 0.05 µg/mL	Week 4 0.05 µg/mL	Week 3 % Recovery	Week 4 % Recovery
Dichlorvos	0.0511	0.0464	102	93
Dimethoate OA	0.0529	0.0506	106	101
Dimethoate	0.0530	0.0497	106	99
Diazinon OA	0.0470	0.0454	94	91
Diazinon	0.0466	0.0430	93	86
Malathion OA	0.0467	0.0463	93	93
Malathion	0.0463	0.0490	93	98
Chlorpyrifos OA	0.0540	0.0529	108	106
Chlorpyrifos	0.0477	0.0454	95	91
DEF	0.0517	0.0491	103	98
Phosmet	0.0518	0.0474	104	95

19. Revision History

	Date	Updated Revision	Original Procedure
1	Description: New SOP for the analysis of Selected Organophosphates		
	7/31/18		Standard Operating Procedure for the Determination of Selected Organophosphate Pesticides Collected On XAD-2 by Gas Chromatography Triple Quadrupole Mass Spectrometry

20. References

20.1. NLB Laboratory Quality Control Manual, Revision 3.0 2015

20.2. NLB Chemical Hygiene Plan, current version

20.3. Determination of Selected Pesticides Collected on XAD-4 Resin by Ultra Performance Liquid Chromatography Mass Spectrometry and Gas Chromatography Mass Spectrometry, Revision 2, California Department of Food and Agriculture 3/28/2012

20.4. Thermo Scientific AI 1310/AS 1310 Autosamplers User Guide

20.5. Thermo Scientific TRACE 1300 and TRACE 1310 Gas Chromatographs User Guide

20.6. Thermo Scientific TSQ 8000 Evo Mass Spectrometer User Guide

20.7. Thermo Scientific TSQ 8000 Evo Mass Spectrometer Auto SRM User Guide

20.8. Thermo Scientific Chromeleon 7.2 Quick Start Guide

To: Michael Werst, Chief
Northern Laboratory Branch

From: Manisha Singh, Ph.D. MS
Chief, Quality Management Branch

Date: June 23, 2020

Subject: STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF SELECTED ORGANOPHOSPHATE PESTICIDES COLLECTED ON XAD-2 RESIN BY GAS CHROMATOGRAPHY-TRIPLE QUADRUPOLE MASS SPECTROMETRY

Thank you for the submission of the addendum (see attached) to the Standard Operating Procedure (SOP) for the Determination of Selected Organophosphate Pesticides Collected on XAD-2 Resin by Gas Chromatography-Triple Quadrupole Mass Spectrometry. The Quality Management Section has reviewed the addendum along with the SOP and determined that it covers all of the required elements. None of the changes listed in the addendum impact the completeness of the previously approved SOP version. Included is the SOP Review Checklist for reference. The addendum is approved.

Please direct comments or questions to Kyle Vagadori at (916) 445-9391 or my email at kyle.vagadori@arb.ca.gov.

Attachment(s)

cc: Greg Gilani, Manager
Quality Management Section

Patrick Rainey, Manager
Organic Laboratory Section

Kyle Vagadori
Quality Management Section

State of California
California Environmental Protection Agency
Air Resources Board
MLD/QMS-066 (NEW 4/14)

QUALITY MANAGEMENT DOCUMENT ADDENDUM

(District completes Sections 1 through 6 -- please type)

Section 1. ARB Document
☐ Quality Management Plan (QMP)
☐ Quality Assurance Project Plan (QAPP)
☒ Standard Operating Procedure (SOP)

Section 2. Submitter Information		
Submitter Name:	Verna Brock	
Submitter Signature/Date:	VMB	6-11-20

Section 3. Document Title *(specify exact title, revision #, and date of ARB Document(s) that your District proposes to modify)*	**Date**
SOP MLD077 Revision Number 0.0	7/31/2018

Section 4. Proposed Deviation(s)
(specify exact section(s), page number(s) and language in existing ARB document that your District proposes to modify and then specify proposed modification (including any spreadsheets or forms).

Section 9 Equipment and Supplies

9.1. Gas Chromatograph: system with programmable oven, electronic pressure control for capillary columns with safety feature shutdown when gas pressures falls below set levels, programmable heated injector, and automated liquid injector

9.2. Column: Thermo TG-5 SilMS, 30 meter, 0.25 mm inner diameter, 0.25 µm film thickness, or equivalent

9.3. Detector: MS/MS

9.4. Syringe Filters: Disposable PTFE 0.2 µm Filter (13 mm -25 mm GD/X)

9.5. Disposable Syringes: 3 mL volume such as BD disposable syringes part# 309656

9.6. 4 mL glass storage vials with Teflon lined screw caps

9.7. Ultrasonic bath: capable of temperature programing such as Branson model 8510

9.8. 8 mL glass extraction vials

9.9. Autosampler deactivated vials with cap

9.10. Autosampler 250 µL flat bottom inserts

9.11. Volumetric Flasks: 5 mL, 10 mL, 25 mL, 50 mL, and 100 mL volume ranges

9.12. XAD-2 resin tubes: 400/200 (mg) such as SKC catalog # 226-30-06

9.13. Analytical balance capable of weighing as low as 0.1 mg

9.14. Eppendorf electronic pipettes: 15 - 5000 µL volume ranges

9.15. 1.5 mL disposable Pasteur pipettes

9.16. Tweezers

9.17. Hand-held glass cutter

9.18. Disposable nitrile or neoprene gloves to handle organic solvents

9.19. Hamilton microliter syringes (or equivalent): 10 µL, 25 µL, 250 µL, 500 µL, and 1000 µL volume ranges

ARB modification to Section 9 – Equipment and Supplies

9.1. Gas Chromatograph: system with programmable oven, electronic pressure control for capillary columns with safety feature shutdown when gas pressures falls below set levels, PTV (Programmed Temperature Vaporizing) inlet, and automated liquid injector

9.2. Column: Thermo TG-5 SilMS, 30 meter, 0.25 mm inner diameter, 0.25 µm film thickness, or equivalent

9.3. Detector: MS/MS

9.4. PTV inlet liner, 2mm x 2.75mm x 120mm, such as Thermo Scientific catalog #453T2120

9.5. GC inlet septa, 11mm, such as Thermo Scientific catalog #313G3230

9.6. Syringe Filters: Disposable PTFE 0.2 µm Filter (13 mm -25 mm GD/X)

9.7. Disposable Syringes: 3 mL volume such as BD disposable syringes part# 309656

9.8. 4 mL glass storage vials with Teflon lined screw caps

9.9. Ultrasonic bath: capable of temperature programing such as Branson model 8510

9.10. 8 mL glass extraction vials

9.11. Autosampler deactivated vials with cap

9.12. Autosampler 250 µL flat bottom inserts

9.13. Volumetric Flasks: 5 mL, 10 mL, 25 mL, 50 mL, and 100 mL volume ranges

9.14. XAD-2 resin tubes: 400/200 (mg) such as SKC catalog # 226-30-06

9.15. Analytical balance capable of weighing as low as 0.1 mg

9.16. Eppendorf electronic pipettes: 15 - 5000 µL volume ranges

9.17. 1.5 mL disposable Pasteur pipettes

9.18. Tweezers

9.19. Hand-held glass cutter

9.20. Disposable nitrile or neoprene gloves to handle organic solvents

9.21. Hamilton microliter syringes (or equivalent): 10 µL, 25 µL, 250 µL, 500 µL, and 1000 µL volume ranges

Section 13.2.1 Analytical Sequence

Each analytical batch of 10 or fewer samples must include bracketing standards, controls, replicates, and blanks as listed below. A 0.7 µL injection volume is used for all analyses. The recommended order of analysis is as follows:

- Solvent blank
- Calibration standards
- Control standard
- Solvent blank
- Laboratory Control Spike
- Method Blank
- Samples (up to 10 including breakthrough analyses)
- Breakthrough analysis (one every 10 or fewer samples)
- Replicate (one every 10 or fewer samples)
- Solvent blank
- CCV standard

ARB modification to Section 13.2.1 – Analytical Sequence

Each analytical batch of 10 or fewer samples must include bracketing standards, controls, replicates, and blanks as listed below. A 1.0 µL injection volume is used for all analyses. The recommended order of analysis is as follows:

- Solvent blank
- Calibration standards
- Control standard
- Solvent blank
- Laboratory Control Spike
- Method Blank
- Samples (up to 10 including breakthrough analyses)
- Breakthrough analysis (one every 10 or fewer samples)
- Replicate (one every 10 or fewer samples)
- Solvent blank

- CCV standard

Section 13.2.2 GC-MS/MS Analytical Conditions

GC:

- Thermo Fisher Scientific GC Trace 1310
- Liner: Baffled PVT 2mm x 2.75mm x 120mm
- Injector: 275 °C
- Flow mode: Constant flow
- Split Mode: CT splitless
- Column: Thermo TG-5 SilMS, 30 meter, 0.25 mm inner diameter, 0.25 µm film thickness
- GC Temperature Program: Oven initial 55 °C, hold 4 min, Ramp to 200 °C at 10 ˚C/min, ramp to 260 °C at 20 °C /min
- Total run time 22.5 minutes
- Splitter open at 1 min
- Carrier Gas: UHP Helium
- Column Flow: Helium, 1.5 mL/min, 93.5 kPa
- Splitter: 10 mL/min

MS/MS:

- Ionization Mode: Electron Ionization Positive Mode
- Collision Gas: UHP Argon
- Acquisition Mode: Selective Reactive Monitoring
- Tuning: PFTBA on masses 69, 131, 219, 414, 502
- Transfer line temperature 250 °C

Run parameters and MS quantitation ions for each compound are listed in Table 2 and Table 3.

Table 2. MS/MS Run Parameters

Compound	Retention Time (min)	Scan Window (min)	Precursor Mass (m/z)	Product Mass (m/z)	Collision Energy (eV)
Dichlorvos	9.01 9.01	0.5 0.5	109 185	79 93.1	5 10
Dimethoate OA	11.42 11.42 11.42	1.5 1.5 1.5	156.1 156.1 156.1	79.1 80.1 110.1	20 15 10
Dimethoate	12.35 12.35 12.35	1.25 1.25 1.25	87 93 125	42.1 63.1 79.1	10 10 10
Diazinon OA	12.53 12.53 12.53	0.5 0.5 0.5	137.1 217.1 273.2	84.1 119.1 137.2	10 10 10

Diazinon	12.72	0.5	137.1	84.1	10
	12.72	0.5	152.2	137.2	10
Malathion OA	13.39	0.5	99.1	71.1	10
	13.39	0.5	127.1	99.1	5
	13.39	0.5	127.1	109.1	10
Malathion	13.94	0.5	127.1	99.1	5
	13.94	0.5	173.1	99.1	15
Chlorpyrifos OA	13.97	0.5	197	169	10
	13.97	0.5	242	150	20
	13.97	0.5	270	242	10
Chlorpyrifos	14.08	0.5	257.9	166	20
	14.08	0.5	257.9	194	15
	14.08	0.5	314.1	258	15
DEF	15.67	0.5	147	113	10
	15.67	0.5	169.1	57.1	10
	15.67	0.5	202	147	5
Phosmet	17.78	0.5	160.1	77.1	20
	17.78	0.5	160.1	133.1	10

Table 3. MS/MS Quantitation Ions

Compound	Quantitation Ion
Dichlorovos	93.1
Dimethoate OA	110.10
Dimethoate	42.10
Diazinon OA	84.10
Diazinon	84.10
Malathion OA	71.00
Malathion	99.10
Chlorpyrifos OA	242.00
Chlorpyrifos	166.00
DEF	147.00
Phosmet	77.10

ARB modification to section 13.2.2 – GC-MS/MS Analytical Conditions

GC:

- Thermo Fisher Scientific GC Trace 1310
- PTV inlet parameters: injection temperature 50 °C (hold 0.05 min), transfer ramp 14.5 °C/sec to 275 °C (hold 0.50 min), cleaning phase ramp 14.5 °C/sec to 295 °C (hold 5.00 min at 75.0mL/min). Post cycle temperature: cool down
- Operating Mode: splitless
- Split flow: 26.0 mL/min
- Splitless time: 1.00 min
- Purge flow: 5.00 mL/min
- Constant septum purge: on

- Vacuum compensation: on
- Column: Thermo TG-5 SilMS, 30 meter, 0.25 mm inner diameter, 0.25 µm film thickness
- GC Temperature Program: Oven initial 55 °C, hold 4.0 min, Ramp to 260 °C at 25 ˚C/min
- Total run time 16.0 minutes
- Carrier Gas: UHP Helium
- Column Flow: 1.5 mL/min constant flow

MS/MS:

- Ionization Mode: Electron Ionization Positive Mode
- Collision Gas: UHP Argon
- Acquisition Mode: Selective Reactive Monitoring
- Tuning: PFTBA on masses 69, 131, 219, 414, 502
- Transfer line temperature 245 °C
- Ion source temperature 250 °C

Run parameters and MS quantitation ions for each compound are listed in Table 2 and Table 3.

Table 2. MS/MS Run Parameters

Compound	Retention Time (min)	Scan Window (min)	Precursor Mass (m/z)	Product Mass (m/z)	Collision Energy (eV)
Dichlorvos	8.30	0.5	109 185 186.9	79 93 93	6 12 12
Dimethoate OA	10.20	0.5	156.1 156.1 156.1	79.1 80.1 110.1	20 15 10
Dimethoate	10.90	0.5	87 93 125	42.1 63 79	10 8 8
Diazinon OA	11.00	0.5	137 137 273.1	54.1 84.1 137.1	20 12 12
Diazinon	11.10	0.5	137.1 137.1 179.1	54.1 84.1 121.5	20 12 26
Malathion OA	11.50	0.5	99 127 127	71 99 109	8 6 12
Malathion	11.85	0.5	92.8 125 173.1	63 79 99	8 8 12

Chlorpyrifos OA	11.87	0.5	108.9 108.9 269.8	81 91 242	8 6 6
Chlorpyrifos	11.93	0.5	196.7 196.7 313.9	107 168.9 257.9	36 12 12
DEF	12.80	0.5	169.3 202 202	57.1 112.9 147	6 16 6
Phosmet	14.30	0.5	160 160 160	50.9 76.9 133	38 22 10

Table 3. MS/MS Quantitation Ions

Compound	Quantitation Ion
Dichlorovos	109
Dimethoate OA	156.1
Dimethoate	87
Diazinon OA	137
Diazinon	137.1
Malathion OA	99
Malathion	92.8
Chlorpyrifos OA	108.9
Chlorpyrifos	196.7
DEF	169.3
Phosmet	160

Section 5. Justification for Deviation(s) *(provide explanation of why modification(s) to existing ARB document is necessary)*
Section 9: added additional instrument consumables Section 13: updated and optimized instrument operating parameters as a result of new knowledge gleaned via Thermo training.

Section 6. Attachment(s) ☐ *(specify attachment titles and number of pages, include modified spreadsheets or forms)*	**# of Pages**

Section 7. ARB Approval *(completed by ARB)*		
Name/Phone Number:	Greg Gilani	916-323-2915
Title:	ARS I	
Signature/Date:	Greg Gilani	6/17/2020
Addendum Number	A33	

Completed form must be scanned/emailed or mailed to:

Mr. Greg Gilani
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