Appendix J. Chemical Analytical Method for Group 1 Candidate Pesticides Using Gas Chromatography, UCD Trace Analytical Laboratory

TAL Laboratory Standard Operating Procedure for the Multiresidue Analysis of Air Samples from the Lompoc Region, 5/15/2000

A. Arrival of Samples at the Laboratory

1. Check chain of custody against samples received at the laboratory.
2. Log sample information, including sample condition into a computer database and assign a unique laboratory sample number to each sample.
3. Xerox chain of custody documents and provide a copy to ARB personnel.
4. If the samples are not to be extracted immediately, place samples in a freezer with a temperature range of approximately -10 to -20 °C.
5. Resin samples for oxydemeton-methyl analysis will be stored at -10 to -20 °C for analysis at a later date.

B. Sample Extraction

1. Remove Teflon cap and screen from resin cartridge and pour resin into an appropriate jar. Carefully rinse cartridge with 75 mL of EtOAc and add the solvent to the jar. Cap the jar with a Teflon lined lid.
2. Prepare one laboratory control sample by adding 30 mL of clean XAD-4 resin to a 125 mL wide mouth jar. Add 75 mL of ethyl acetate and cap the jar.
3. Prepare three laboratory concurrent resin fortification samples by add 30 mL of clean XAD-4 resin to an appropriate jar and fortifying the resin with a standard mixture of a known concentration using an appropriate syringe. Fortifications will be between 1 -5 times the estimated quantitaion limit (EQL). Add 75 mL of ethyl acetate and cap the jar.
4. Mechanically swirl for one hour, on a rotary platform shaker, at a moderate speed.

C. Sample Work up

Analysis for Compounds other than Oxydemeton Methyl

1. Quantitatively transfer 37.5 mL to a 100 mL round bottom flask and evaporate the solvent to dryness using a rotary evaporator.
2. Add 2.0 mL of ethyl acetate to the flask, cap and swirl.
3. Transfer an aliquot from the flask to a GC vial and inject on the GC/FPD analytical system or the GC/MSD.
4. Inject 3 µL of sample for GC/FPD or 2 µL of sample for GC/MSD, along with the appropriate standard concentrations for each of the parent listed in Table I (and oxons where appropriate), into the gas chromatograph. If the peak height/area for either the parent or the oxon is larger than 110% of the highest standard, dilute the sample with ethyl acetate and re-inject.
5. Calculate the mass of the compound in µg, based on the linear regression curve for TurboChrom® and the appropriate dilution factors.
   Concentration (µg/mL) x Dilution Factor (mL)/Sample = µg/sample.

Analysis for Total Oxydemeton-Methyl as Dioxydemeton-Methyl

1. Extract samples as per "B" above.
2. Quantitatively transfer 37.5 mL to a 100 mL round bottom flask and evaporate the solvent to dryness using a rotary evaporator.
3. Add 2 mL of acetone.
4. Add 5 mL of 20% magnesium sulfate solution and swirl.
5. Add 20 mL of 0.5N potassium permanganate solution and swirl. Allow sample to sit for 30 minutes with occasional swirling.
6. Transfer the oxidized mixture to a 125 mL separatory funnel.
7. Rinse the oxidation flask with 20 mL of chloroform and add to the separatory funnel.
8. Shake the funnel for 30 seconds to extract & allow the phases to separate.
9. Drain the lower layer (chloroform) through No. 541 filter paper containing a small amount of granular, anhydrous sodium sulfate into a 100 mL boiling flask.
10. Repeat the extraction twice more with 20 mL portions of chloroform.
11. Rinse the sodium sulfate with 5 mL of chloroform.
12. Evaporate the combined extracts just to dryness on a rotary vacuum evaporator.
13 Add 2.0 mL of ethyl acetate to the flask, cap and swirl the flask. Transfer an aliquot from the flask to a GC vial and analyze using the GC-FPD analytical system.
14. Inject 3 µL of sample, along with the appropriate standard concentrations of dioxydemeton-methyl into the gas chromatograph. If the peak height of the sample is larger than the highest standard, dilute the sample with ethyl acetate and re-inject.
15. Calculate the mass of the oxidized oxydemeton-methyl in µg, based on the linear regression curve for TurboChrom® and the appropriate dilution factors.
    Concentration (µg/mL) x Dilution Factor (mL)/Sample = µg/sample.
16. Calculate the total parent in each sample using the following equation:
    Total Parent =Total oxidized oxdemeton-methyl x ratio of mass to corresponding oxon.

D. **Analysis**

Tables I through III give the analyte, the corresponding analytical system, and the typical parameters for each system.

Table I

					MSD Macro Information		
Compound	Detector	Retention Time (min)	Quantitation ion	Confirmation Ion	Register	Window	Page/ window
EPTC	MSD	9.44	189	132	R0	5	1, 1
Ethalfluralin	MSD	12.5	276	292	R1	6	1, 2
Trifluralin	MSD	12.5	306	264	R2	7	1, 3
Cycloate	MSD	13.4	154	215	R3	8	1, 4
Pronamide	MSD	15.0	173	175	R4	9	1, 5
PCNB	MSD	15.4	237	295	R5	10	1, 6
Simazine	MSD	15.6	201	203	R6	12	2, 1
Dicloran	MSD	15.6	206	208	R7	11	2, 2
Vinclozolin	MSD	16.4	285	287	R8	13	2, 3
Chlorothalonil	MSD	16.8	266	264	R9	14	2, 4
Mefenoxam	MSD	17.3	206	279	R10	15	2, 5
Metolachlor	MSD	17.4	238	240	R11	16	2, 6
Chlorthal-dimethyl	MSD	17.6	301	299	R12	17	3, 1
Iprodione	MSD	22.1	244	246	R15	20	3, 4
Dicofol	MSD	18.1, 22.9	139	250,251	R13,16	18,21	3,2 3,5
Permethrin	MSD	24.9, 25.2	183	163	R17	22	3, 6
Diazinon	FPD						
Naled	FPD						
Fonofos	FPD						
Fonofos oxon	FPD						
Diazinon oxon	FPD						
Chlorpyrifos	FPD						
Dimethoate oxon	FPD						
Dimethoate	FPD						
Malathion	FPD						
Chlorpyrifos oxon	FPD						
Malathion oxon	FPD						
Oxydemeton-methyl	FPD						

Table II. Instrumental Parameters for the ITEH GC/FPD System
(Typical Parameters)

Instrument: Hewlett Packard 5890A
Detector: Flame Photometric, Phosphorus Mode

Inlet: Packed/Megabore

Injection System: HP-7673 Autosampler, 3 µL injection

Column: 30 m x 0.53 mm DB-210 J & W Scientific Mega-bore capillary column, 1.0 µm film

Temperatures	Injector	250 °C	
	Detector	225 °C	
	Column	$Temp_1$	170 °C
		$Hold_1$	0.5 min
		$Rate_1$	5.0 °C /min
		$Temp_2$	200 °C
		$Rate_2$	8 °C /min
		$Temp_3$	225 °C
		Hold	4.0 min
Gas Flows:	Carrier (He)	12.1	mL/min
	Air	101	mL/min
	Hydrogen	79	mL/min

Prior to analysis, the analyst will inject calibration standards to check gas chromatograph performance.

Data System: Perkin-Elmer TurboChrom® Version 6.01

Table III. Instrumental Parameters for the GC/MSD System
(Typical Parameters)

Instrument: Hewlett Packard 6890
Detector: Mass Selective Detector (MSD)Model 5972A, Selective Ion Monitoring (SIM) Mode

Inlet: Pulsed Splitless mode

Injection System: HP-7673 Autosampler, 2 µL injection

Column: 30 m x 0.25 mm DB 17ms, J & W Scientific
capillary column, 0.25 µm film

Temperatures	Injector	250 °C
	MSD Couple	280 °C
	Column	$Temp_1$ 70 °C
		Hold 0 min
		$Rate_1$ 10 °C /min
		$Temp_2$ 280 °C
		Hold 4 min

Gas Flows: Carrier (He) 1.0 mL/min Constant flow

Prior to analysis, the analyst will perform a daily Autotune of the MSD to ensure proper MSD function. In addition calibration standards will be injected to check gas chromatograph performance.

Data System: Hewlett-Packard ChemStation® G1701BA. Version B.01.00

ARB/Lompoc Study Phase II
Storage Stability Day 0
Date Fortified: 3/18/00, Date Analyzed: 3/19/00

	Storage	Concurrents					Storage Stability						
	Days	#1	#2	#3	Average	Std Dev.	#1	#2	#3	#4	#5	Average	Std Dev.
Chlorpyifos Oxon	0	94	98	92	95	3.1	99	84	82	81	85	86	7.3
Chlorthal-dimethyl	0	100	103	100	101	1.5	101	98	94	98	95	97	2.7
Cycloate	0	96	97	94	96	1.5	95	88	85	89	86	89	3.7
Diazinon Oxon	0	100	102	100	101	1.2	108	82	85	82	83	88	11.2
Dicloran	0	100	102	97	100	2.5	98	89	82	88	85	88	6.0
Dicofol	0	86	84	79	83	3.5	81	77	75	79	78	78	2.3
Dimethoate Oxon	0	102	104	98	101	3.1	110	83	85	83	82	89	12.0
EPTC	0	95	97	95	95	1.0	96	90	88	92	89	91	3.0
Ethalfluralin	0	97	96	91	95	3.1	91	82	79	84	81	83	4.7
Fonofos Oxon	0	97	99	97	98	1.2	104	84	83	82	84	87	9.3
Iprodione	0	116	109	102	109	7.1	100	87	82	87	85	88	7.0
Malathion	0	102	101	99	101	1.5	108	87	86	84	85	90	10.1
Malathion Oxon	0	98	100	97	98	1.5	104	86	85	82	85	88	8.8
Mefenoxam	0	102	103	98	101	2.5	98	90	87	91	88	91	4.4
Metolachlor	0	103	103	99	102	2.3	99	92	89	94	90	93	3.9
PCNB	0	95	97	92	95	2.4	93	86	82	87	85	87	4.2
Pronamide	0	100	102	96	99	3.0	95	85	80	85	83	85	5.5
Simazine	0	101	105	101	102	2.4	102	97	90	96	92	95	4.8
Trifluralin	0	98	98	93	96	2.6	93	84	81	85	83	85	4.6
Vinclozolin	0	102	104	100	102	1.8	99	92	88	93	91	93	4.2

ARB/Lompoc Study Phase II
Storage Stability Day 31
Date Fortified: 3/18/00 Date Extracted: 4/18/00, 4/20/00 Date Analyzed:4/18/00, 4/20/00

	Storage	Concurrents					Storage Stability						
	Days	#1	#2	#3	Average	Std Dev.	#1	#2	#3	#4	#5	Average	Std Dev.
Chlorpyifos Oxon	31	99	98	98	98	0.6	98	87	87	88	87	89	4.8
Chlorthal-dimethyl	33	92	89	89	90	1.6	91	89	93	94	91	92	1.8
Cycloate	33	113	109	110	111	1.9	113	110	114	115	112	113	2.2
Diazinon Oxon	31	98	99	96	98	1.5	99	89	88	89	89	91	4.6
Dicloran	33	87	83	83	85	2.2	85	82	84	87	85	85	2.1
Dicofol	33	85	85	85	85	0.3	72	71	76	76	76	74	2.4
Dimethoate Oxon	31	96	96	95	96	0.6	100	87	87	87	88	90	5.7
EPTC	33	106	102	104	104	2.1	107	103	108	109	106	107	2.1
Ethalfluralin	33	100	96	95	97	2.4	97	94	94	100	97	96	2.4
Fonofos Oxon	31	95	96	94	95	1.0	97	86	87	86	89	89	4.6
Iprodione	33	82	81	78	80	2.0	89	86	89	93	90	89	2.6
Malathion	31	101	100	98	100	1.5	102	86	89	90	91	92	6.1
Malathion Oxon	31	105	106	104	105	1.0	98	88	89	90	89	91	4.1
Mefenoxam	33	90	87	87	88	1.6	91	88	91	93	90	91	1.9
Metolachlor	33	89	87	87	88	1.4	89	87	91	93	89	90	2.0
PCNB	33	85	82	83	83	1.6	83	83	81	84	85	83	1.5
Pronamide	33	89	86	85	86	2.1	88	85	89	89	86	87	1.9
Simazine	33	107	104	105	105	1.6	91	89	93	95	92	92	2.2
Trifluralin	33	99	94	95	96	2.3	96	93	94	98	95	95	2.0
Vinclozolin	33	96	94	94	95	1.6	91	89	92	95	91	92	1.9

Mefenoxam

Validation (50 µg)

	Replicate			Percent Recovery	
Control	#1	#2	#3	Average	Std Dev.
<1.0	55.5	53.1	52.1	107	3.5

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	2.8	40.6	<1	43.5	87
Rep 2	8.0	38.2	<1	46.1	92
Rep 3	3.4	43.5	<1	46.8	94
Rep 4	1.6	43.8	<1	45.4	91
Average =	3.9	41.5	<1	45.4	91

PCNB

Validation (50 µg)

	Replicate			Percent Recovery	
Control	#1	#2	#3	Average	Std Dev.
<1.0	52.3	49.7	48.1	100	4.2

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	<1	44.2	<1	44.2	88
Rep 2	<1	46.5	<1	46.5	93
Rep 3	<1	48.3	<1	48.3	97
Rep 4	<1	47.9	<1	47.9	96
Average =	<1	46.7	<1	46.7	93

Ethalfluralin

Validation (50 µg)

	Replicate			Percent Recovery	
Control	#1	#2	#3	Average	Std Dev.
<1.0	57.4	54.9	52.1	110	5.3

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	<1	28.3	<1	28.3	57
Rep 2	<1	31.5	<1	31.5	63
Rep 3	<1	30.2	<1	30.2	60
Rep 4	<1	29.1	<1	29.1	58
Average =	<1	29.8	<1	29.8	60

Chlorthal-Dimethyl

Validation (50 µg)

	Replicate			Percent Recovery	
Control	#1	#2	#3	Average	Std Dev.
<1.0	53.4	51.6	50.3	104	3.1

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	<1	11.2	39.1	50.3	101
Rep 2	<1	17.4	34.9	52.3	105
Rep 3	<1	13.2	39.7	52.9	106
Rep 4	<1	8.6	43.8	52.4	105
Average =	<1	12.6	<1	52.0	104

Pronamide

Validation (50 µg)

Control	Replicate #1	#2	#3	Percent Recovery Average	Std Dev.
<1.0	51.8	49.9	50.8	102	1.9

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	11.2	39.1	<1	50.3	101
Rep 2	17.4	34.9	<1	52.3	105
Rep 3	13.2	39.7	<1	52.9	106
Rep 4	8.6	43.8	<1	52.4	105
Average =	12.6	39.4	<1	52.0	104

Iprodione

Validation (50 µg)

Control	Replicate #1	#2	#3	Percent Recovery Average	Std Dev.
<1.0	43.7	42.8	46.6	89	4.0

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	41.7	0.4	<1	42.1	84
Rep 2	35.1	4.4	<1	39.5	79
Rep 3	38.2	3.7	<1	41.9	84
Rep 4	38.8	1.5	<1	40.4	81
Average =	38.5	2.5	<1	41.0	82

Metolachlor

Validation (50 µg)

Control	Replicate #1	#2	#3	Percent Recovery Average	Std Dev.
<1.0	52.7	50.3	52.1	103	2.5

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	7.7	37.3	<1	44.9	90
Rep 2	8.4	38.5	<1	46.9	94
Rep 3	7.6	38.5	<1	46.1	92
Rep 4	7.0	40.3	<1	47.3	95
Average =	7.7	38.6	<1	46.3	93

Metolachlor

Validation (50 µg)

Control	Replicate #1	#2	#3	Percent Recovery Average	Std Dev.
<1.0	56.9	54.1	60.9	115	6.9

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	36.5	14.7	<1	51.2	102
Rep 2	23.3	28.1	<1	51.4	103
Rep 3	31.0	19.7	<1	50.7	101
Rep 4	31.4	20.2	<1	51.6	103
Average =	30.5	20.7	<1	51.2	102

Cycloate

Validation (50 µg)

	Replicate			Percent Recovery	
Control	#1	#2	#3	Average	Std Dev.
<1.0	52.1	50.9	49.8	102	2.3

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	<1	19.3	<1	19.3	39
Rep 2	<1	21.7	<1	21.7	43
Rep 3	<1	17.5	<1	17.5	35
Rep 4	<1	14.5	<1	14.5	29
Average	<1	18.3	<1	18.3	37

Dicloran

Validation (50 µg)

	Replicate			Percent Recovery	
Control	#1	#2	#3	Average	Std Dev.
<1.0	53.9	51.3	48.4	102	5.4

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	11.9	32.7	<1	44.6	89
Rep 2	16.6	28.6	<1	45.2	90
Rep 3	13.9	33.2	<1	47.1	94
Rep 4	9.9	39.0	<1	48.9	98
Average =	13.1	33.4	<1	46.4	93

EPTC

Validation (50 µg)

	Replicate			Percent Recovery	
Control	#1	#2	#3	Average	Std Dev.
<1.0	49.9	48.4	50.3	99	2.0

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	<1	27.0	<1	27.0	54
Rep 2	<1	27.5	<1	27.5	55
Rep 3	<1	26.1	<1	26.1	52
Rep 4	<1	25.2	<1	25.2	50
Average =	<1	26.5	<1	26.5	53

Vinclozolin

Validation (50 µg)

Control	Replicate #1	#2	#3	Percent Recovery Average	Std Dev.
<1.0	50.1	48.5	49.5	99	1.6

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	3.9	40.4	<1	44.3	89
Rep 2	3.9	40.1	<1	44.1	88
Rep 3	3.2	40.9	<1	44.1	88
Rep 4	2.5	43.3	<1	45.9	92
Average =	3.4	41.2	<1	44.6	89

Trifluralin

Validation (50 µg)

Control	Replicate #1	#2	#3	Percent Recovery Average	Std Dev.
<1.0	49.4	45.9	47.4	95	3.5

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	<1	38.8	<1	38.8	78
Rep 2	<1	37.5	<1	37.5	75
Rep 3	<1	40.0	<1	40.0	80
Rep 4	<1	43.3	<1	43.3	87
Average =	<1	39.9	<1	39.9	80

Simazine

Validation (50 µg)

	Replicate			Percent Recovery	
Control	#1	#2	#3	Average	Std Dev.
<1.0	46.6	45.6	49.5	94	4.1

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	39.71359	6.5	<1	46.2	92
Rep 2	30.3201	15.2	<1	45.5	91
Rep 3	34.09429	10.6	<1	44.7	89
Rep 4	34.5	9.2	<1	43.7	87
Average =	34.7	10.3	<1	45.0	90

Dimethoate Oxon

Validation (50 µg)

	Replicate			Percent Recovery	
Control	#1	#2	#3	Average	Std Dev.
<1.0	49.8	53.2	56.4	106	6.6

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	6.9	36.7	<1	43.7	87
Rep 2	3.9	39.7	<1	43.6	87
Rep 3	18.8	26.4	<1	45.2	90
Rep 4	11.9	35.0	<1	47.0	94
Average =	10.4	34.5	<1	44.9	90

Fonofos Oxon

Validation (50 µg)

	Replicate			Percent Recovery	
Control	#1	#2	#3	Average	Std Dev.
<1.0	50.9	52.2	54.1	105	3.2

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	<1	41.9	<1	41.9	84
Rep 2	<1	43.4	<1	43.4	87
Rep 3	<1	43.2	<1	43.2	86
Rep 4	<1	46.1	<1	46.1	92
Average =	<1	43.7	<1	43.7	87

Diazinon Oxon

Validation (50 µg)

	Replicate			Percent Recovery	
Control	#1	#2	#3	Average	Std Dev.
<1.0	55.1	53.7	57.8	111	4.2

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	<1	43.3	<1	43.3	87
Rep 2	<1	42.8	<1	42.8	86
Rep 3	1.1	44.5	<1	45.6	91
Rep 4	<1	45.9	<1	45.9	92
Average =	<1	44.1	<1	44.4	89

Malathion Oxon

Validation (50 µg)

	Replicate			Percent Recovery	
Control	#1	#2	#3	Average	Std Dev.
<1.0	54.0	54.6	55.2	109	1.2

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	13.5	37.5	<1	51.0	102
Rep 2	8.4	45.3	<1	53.7	107
Rep 3	26.6	23.0	<1	49.7	99
Rep 4	18.6	35.2	<1	53.7	107
Average =	16.8	35.3	<1	52.0	104

Malathion

Validation (50 µg)

	Replicate			Percent Recovery	
Control	#1	#2	#3	Average	Std Dev.
<1.0	52.2	53.0	55.4	107	3.3

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	9.6	30.6	<1	40.2	80
Rep 2	5.6	34.3	<1	39.9	80
Rep 3	23.8	21.9	<1	45.7	91
Rep 4	15.3	30.2	<1	45.5	91
Average =	13.6	29.2	<1	42.8	86

Chlorpyrifos Oxon

Validation (50 µg)

	Replicate			Percent Recovery	
Control	#1	#2	#3	Average	Std Dev.
<1.0	47.5	50.7	54.3	102	6.8

Trapping (50 µg added to glass wool)

	Wool	Primary	Backup	Total	% Recovery
Control	<1	<1	<1	<3	<6%
Rep 1	2.3	25.2	<1	27.5	55
Rep 2	1.5	30.2	<1	31.6	63
Rep 3	7.4	18.9	<1	26.3	53
Rep 4	4.6	26.5	<1	31.1	62
Average =	4.0	25.2	<1	29.1	58