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EN-CAS Method No. ENC-4/93

Analytical Method for the Gas Chromatographic Determination of Malathion and Malaoxon Residues in Oranges When Using Continuous Automated Sample Injections

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1.0 INTRODUCTION

1.1 Scope

This method is used for the determination of malathion and malaoxon residues in whole oranges (with the peel included). The limit of quantitation (LOQ) is 0.01 ppm (ug/g) for malathion and malaoxon. Method validation results for oranges are included in this report (see Table I). See Figure 1 for a flowchart of the method.

1.2 Principle

Malathion and its metabolite, malaoxon, are extracted from finely ground whole oranges by blending with acetonitrile for two minutes. Samples are filtered, partitioned with hexanes, and concentrated to 1 to 2 mL using rotary evaporation. Acetone, followed by activated charcoal, is added as a cleanup step. Samples are again filtered and concentrated to incipient dryness using rotary evaporation. The residues are redissolved with dichloromethane/acetone and passed through a disposable silica-gel solid phase extraction cartridge. The eluate is evaporated to dryness, reconstituted with an appropriate volume of acetone-polyethylene glycol, and vortexed. Analyte concentrations are determined by gas chromatography using a flame photometric detector (FPD) operating in the phosphorus mode.

1.2 Principle (continued)

This method is based on and is essentially identical to the American Cyanamic Method M-1886 entitled GC Method for the Determination of Malathion (CL 6.601) and Malaoxon (CL 28.967) Residues in Alfalfa (Green Forage and Hay) When Using Continuous Automated Sample Injections (reference 1). The following modifications have been made:

1. Sample handling procedure: A 10-g representative sample (rather than a 20-g) is weighed into an 8-oz. French square bottle, 100 mL acetonitrile is added, and the sample is blended for two minutes using an Omni-Mixer homogenizer (instead of a blender). The entire aliquot is processed through the method.

2. Silica-gel cleanup: The residues are dissolved in 1 mL acetone followed by 9 mL dichloromethane, and a small amount of sodium sulfate is added to absorb water. The entire procedure is conducted using a vacuum box (rather than using positive pressure).

3. Standard solutions (stock, fortification, and GC) are stored in the freezer (vs refrigerator) when not in use and are stable for six months.

4. Gas chromatography standard solutions: Standards are prepared from higher stock concentrations, using acetone-polyethylene glycol as the dilution solvent, ranging from 0.025 µg/mL up to 1.0 µg/mL.

5. GC column: A J&W DB-5 30-m x 0.32-mm id x 1.0-µm film thickness column is used, instead of an OV-101 packed column.

1.2 Principle (continued)

6. GC conditions: The initial column temperature is 50°C for 0.5 min ramping at 40°C/min to 175°C for 25 min, ramping at 35°C/min to 185°C for 5 min, and finally ramping at 35°C/min to 230°C for 5 min. The inlet temperature is 200°C and detector temperature is 250°C. The American Cyanamid method uses a column oven temperature of 190°C isothermal with a inlet temperature of 250°C and a detector temperature of 275°C.

7. Gas chromatographic analysis: The samples are not analyzed in cuplicate.

2.0 APPARATUS

[NOTE: All apparatus listed may be replaced by equivalent apparatus from alternate sources if experimental verification supports such substitutions.]

2.1 Flasks, 250-mL Erlenmeyer or flat-bottomed boiling, with 24/40 ground glass fittings

2.2 Flasks, 500-mL sidearm

2.3 Filtering funnels, Buchner, porcelain, 100-mm plate diameter

2.4 Separatory funnels, 250-mL, with 24/40 ground glass fittings

2.5 Filter paper, 9-cm GF/C and 12.5-cm 934-AH glass fiber filters, Whatman Inc.

2.6 Stoppers, plastic, 24/40

2.7 TurboVap tubes, 15 mL conical, with plastic snap caps, Zymark Corporation, Cat. No. ZA 7519

2.8 Bottles, 8-ounce French squares, wide mouthed, with Teflon-lined caps

2.9 Solid Phase Extraction Columns, Silica gel, 500-mg, 3 mL, J. T. Baker Chemical Company, Phillipsburg, New Jersey, Cat. No. 7086-3

2.0 APPARATUS (continued)

2.10 GC Column, 30-m x 0.32-mm i.d., DB-5, with 1.0-µm film thickness, J&W Scientific, Cat. No. 123-5033

2.11 Rotary Evaporator: Büchi Rotavapor, model RE-111, Brinkman Instruments, Inc., Westbury, New York

2.12 Vortexer, Pulser Vortexer Test Tube Mixer, model PV6, Glascol, Terre Haute, Indiana

2.13 Integrator, Hewlett-Packard 3396A

2.14 Omni-Mixer, Model No. 17105 Homogenizer, Omni International, Waterbury, Connecticut

2.15 Balance, Analytical, Mettler H20, precision ±0.01 mg

2.16 Balance, Top loading, TL1600 American Scientific Products, precision ±0.01 g

2.17 Microliter syringes, 100-, 250-, 500-, 1000-µl capacity, Hamilton Company

2.18 VacElut SPS24, Analytichem International, Harbor City, California

2.19 TurboVap, LV Evaporator, Zymark Corporation, Hopkinton, Massachusetts

2.20 Gas Chromatograph, Hewlett-Packard 5890 equipped with a flame photometric detector operating in the phosphorus mode.

3.0 REAGENTS

[NOTE: All reagents listed may be replaced by equivalent reagents from alternate sources if experimental verification supports such substitution:]

3.1 Acetonitrile, UV, Burdick and Jackson

3.2 Hexanes, pesticide grade, Fisher

3.3 Acetone, Optima, Fisher

3.4 Methylene chloride, pesticide grade, Fisher

3.0 REAGENTS (continued)

3.5 Sodium sulfate (Na_2SO_4), anhydrous, ACS certified, oven baked at 600°F for 2 hours and cooled to room temperature in a dessicator

3.6 Activated Carbon, Nuchar C-190N, Cat. No. 5790, Eastman Kodak Company

3.7 Polyethylene Glycol, 400, Cat. No. 1363941, Eastman Kodak Company

3.8 Analytical Standards: Analytical grade, known purity, Cheminova Agro A/S

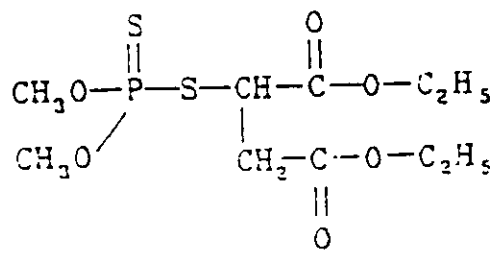
a. Malathion: phosphorodithioic acid, s-,[1,2-bis(ethoxycarbonyl)ethyl]o,o-dimethyl-dithiophosphate

b. Malaoxon: phosphorothioic acid, s-1,2-bis (ethoxycarbonyl)ethyl]o,o-dimethyl ester.

3.9 Acetone-polyethylene glycol: 0.02% in acetone, 200 µl of polyethylene glycol added to 1,000 mL of acetone

4.0 REFERENCE STANDARDS

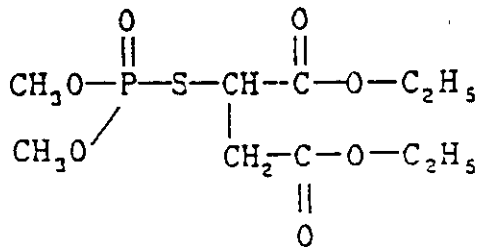
Malathion



$C_{10}H_{19}O_6PS_2$
M.W. 330.4

4.0 REFERENCE STANDARDS (continued)

Malaoxon



$C_{10}H_{19}O_7PS$
M.W. 314.3

5.0 PREPARATION OF ANALYTICAL STANDARDS

5.1 Fortification Standards

Weigh 100 mg (corrected for purity) of reference standard (of known purity, lot number and expiration date) separately for both malathion and malaoxon using an analytical balance. Dissolve and dilute each to a volume of 100 mL with acetone to prepare 1000 µg/mL stock solutions. Prepare a 100 µg/mL combined malathion and malaoxon standard in acetone by aliquoting appropriately from the individual 1000 µg/mL stock solutions. Serially dilute the 100 µg/mL combined standard in acetone to prepare both a 10 µg/mL and 1.0 µg/mL combined malathion and malaoxon standard in acetone.

Use these solutions to fortify control samples in order to monitor procedural recovery for combined malathion and malaoxon.

For individual fortification standards, serially dilute the individual 1000 µg/mL stock solutions to prepare 100-, 10-, and 1.0 µg/mL malathion standards in acetone as well as 100-, 10-, and 1.0 µg/mL malaoxon standards in acetone. Use these solutions to fortify control samples in order to monitor procedural recovery for malathion and malaoxon individually. The stock and fortification standards are stable for at least 6 months. [NOTE: Store all standards in a freezer at -10°C to -17°C.]

5.2 Gas Chromatographic Standards

Combine the appropriate amounts and serially dilute, with 0.02% polyethylene glycol (PEG) in acetone, the 1000 µg/mL malathion and malaoxon stock solutions to prepare both a 100 µg/mL and 25 µg/mL combined standards. Serially dilute the combined standards to prepare a typical range of standards from 0.025 µg/mL to 1.0 µg/mL, in 0.02% PEG in acetone, to be used as gas chromatographic (GC) calibration standards. The use of PEG is necessary to maintain the malaoxon sensitivity over the course of a GC run. The GC calibration standards are stable for 6 months. [NOTE: Store all standard solutions in a freezer at a temperature of -10°C to -17°C.]

6.0 ANALYTICAL PROCEDURES

6.1 Sample Storage and Processing

6.1.1 Sample Storage

Store residue samples (whole or homogenized) frozen in a freezer with a temperature range of -23°C to -17°C.

6.1.2 Sample Processing

Homogenize whole samples by chopping with a Hobart food processor, using dry ice. The samples may require cutting into smaller pieces in order to fit into the Hobart. Clean all cutting tools and Hobart parts thoroughly between samples to prevent cross contamination. After the sample is thoroughly chopped and mixed, place it in the freezer to allow the dry ice to sublime.

6.2 Extraction and Partition

See reference 2 for extraction validation data.

6.2.1 Weigh 10.0 g of homogenized orange sample into an 8-oz. French square bottle. If the sample is to be stored frozen prior to processing, the bottle should be capped tightly with a Teflon-lined cap.

6.2 Extraction and Partition (continued)

6.2.2 Fortify the control sample(s) with the appropriate amount of malathion and/or malaoxon, allowing the solvent to evaporate in a fume hood. Typically 1 or 2 fortifications are analyzed concurrently with each batch of samples to monitor procedural recovery. The level(s) are chosen to reflect anticipated residues found in the samples. Wait no longer than five minutes before proceeding.

6.2.3 Add 100 mL of acetonitrile to the sample and blend for two minutes, using an Omni-Mixer homogenizer, operating at a moderate speed.

6.2.4 Filter the samples, under vacuum, through a 9-cm Whatman GF/C (glass fiber) filter paper placed under a 12.5-cm Whatman 934-AH filter paper, inside a 100-mm Buchner funnel. Collect the extract into a 500-mL sidearm filter flask. Rinse the French square bottle with approximately 10 - 50 mL acetonitrile and filter through the Buchner funnel into the same 500-mL filter flask.

6.2.5 Transfer the entire extract to a 250-mL separatory funnel and partition the acetonitrile with 50 mL of hexanes, shaking for approximately one minute. Allow the layers to separate and transfer the lower, acetonitrile layer into a 250-mL Erlenmeyer flask. Discard the hexanes. Evaporate the sample to 1-2 mL using rotary evaporation with a bath temperature ≤40°C.

6.3 Carbon Cleanup

6.3.1 Dissolve the remaining solution from 6.2.5 in 50 mL acetone. Add 1.0 g of activated carbon and swirl. Allow the mixture to stand 30-40 minutes with occasional gentle swirling.

6.3 Carbon Cleanup (continued)

6.3.2 Vacuum-filter the sample through a 9-cm Whatman GF/C filter paper inside a Buchner funnel. Collect the extract into a 500-mL sidearm filter flask. Rinse the Erlenmeyer flask, Buchner funnel and filter paper with 50 mL acetone, collecting the rinses into the same 500-mL filter flask.

6.3.3 Transfer the extract to a 250-mL Erlenmeyer flask and carefully rotary evaporate the sample to incipient dryness at a bath temperature of ≤40°C. Use a gentle stream of nitrogen to evaporate the solvent just to dryness.

6.4 Silica Gel Cleanup

6.4.1 Dissolve the residual film from 6.3.3 with 1 mL acetone followed by 9 mL dichloromethane (DCM). Add a small amount of Na_2SO_4 (<50 mg) to the sample to absorb water.

6.4.2 Pre-condition a silica gel bond elut by passing 3 mL of 10/90 acetone/DCM through the cartridge, using a Vacflut box with a vacuum setting of 5 psi.

6.4.3 Transfer the sample from 6.4.1, leaving the Na_2SO_4 behind, to the pre-conditioned bond elut, and using a vacuum setting of 5 psi, collect the fraction in a 15-mL TurboVap tube. Rinse the sample flask with 4 mL 10/90 acetone/DCM, transfer to the bond elut, and collect into the same TurboVap tube.

6.5 Final Dilution

6.5.1 Concentrate the sample from 6.4.3 to dryness using a TurboVap Evaporator with a gentle stream of nitrogen at a water bath temperature of ≤30°C.

6.5 Final Dilution (continued)

6.5.2 Reconstitute the sample with a known volume (typically 2 mL for a 0.01 ppm screening level) of 0.02% polyethylene glycol in acetone and vortex the sample for approximately 30 seconds. The sample is now ready for GC analysis. Store samples in a freezer at a temperature of -10°C to -17°C, when necessary, to preserve sample integrity.

6.6 Gas Chromatographic Determinations

Use a 30-m x 0.32-mm, 1.0-µm film thickness, fused silica capillary DB-5 column to achieve gas chromatographic separation. Use a Hewlett-Packard Model 5890-A Gas Chromatograph equipped with a flame photometric detector operating in the phosphorus mode. Gas chromatographic conditions are listed in Section 7.0 of this method.

6.7 Sequence of Analysis

Inject a series of standards (typically 4 or 5) at the beginning of the GC run to check for linearity. Alternate samples and standards so, at least, every fourth injection is a standard. Inject 2 or 3 standards at the end of the run. Vary the concentration of standards injected throughout the run to demonstrate detector linearity. See Table II.

6.8 Safety Precautions

Use normal safety precautions, including the wearing of gloves and safety glasses. The use of a fume hood is necessary to minimize exposure to the analytes and organic solvents used in this procedure.

6.9 Time Required for Analysis

A set of 8-12 samples (including controls and recoveries) can be processed and prepared for injection on the gas chromatograph by one analyst in approximately 1½ 8-hour days. An additional ½ day is required to annotate and calculate the data.

7.0 GAS CHROMATOGRAPHIC ANALYSIS

7.1 Description and Typical Operating Conditions

Instrument:	Hewlett-Packard 5890A with a Flame Photometric Detector operating in the phosphorus mode	
Column:	Fused Silica Capillary DB-5 Column, 30-m x 0.32-mm, 1.0-µm film thickness (J & W Scientific)	
Gases:	Carrier: He at 40 psi - 3.5 mL/min Detector: H_2 at 30 psi - 70 mL/min Air at 50 psi - 115 mL/min Aux. H_2 at 40 psi - 22 mL/min	
Injection Volume:	1 µL	
Temperature:	Injector: 200°C Detector: 250°C	
Column Temperature Conditions:	Initial Temperature: Initial Time: Rate A: Temperature A: Final Time A: Rate B: Temperature B: Final Time B: Rate C: Temperature C: Final Time C:	50°C 0.5 minute 40°/minute 175°C 25 minutes 35°/minute 185°C 5 minutes 35°/minute 230°C 5 minutes
Typical Retention Times:	Malaoxon: Malathion:	23.6 min 29.9 min.

7.1 Description and Typical Operating Conditions (continued)

Typical Integrator Parameters: Hewlett-Packard 3396A

RUN PARAMETERS		INTEGRATOR DEFINITIONS
ZERO	= 10	2. SET BASELINE ALL VALLEYS
ATTENUATION	= 3	8. TURN ON START/STOP MARKS
CHART SPEED	= 0.5 cm/min.	9. TURN OFF INTEGRATION
THRESHOLD	= 1	
PEAK WIDTH	= 0.35 min	

TIMETABLE EVENTS	
0 min CHART SPEED	= 0.0 cm/min.
0 min INTEGRATION #	= 2
0 min INTEGRATION #	= 9
0 min INTEGRATION #	= 8
20 min CHART SPEED	= 0.5 cm/min.
22 min INTEGRATION #	= 8
35 min INTEGRATION #	= 9
40 min STOP	

7.2 Calibration

Use the combined malathion and malaoxon standards in polyethylene glycol-acetone in concentrations ranging from 0.025 µg/mL to 1.0 µg/mL to calibrate the instrument. Inject at least 3 standards at the beginning of the run, after approximately every 2 or 3 samples throughout the run, and at least 2 standards at the end of the run. Generate a linear regression curve using the resulting peak height (obtained from the integrator) vs. nanograms injected. The correlation coefficient for the line should be equal to or greater than 0.990. The nanograms found are determined by inserting the sample peak height values into the standard curve linear regression equation.

7.3 Representative Chromatograms

Typical chromatograms illustrating GC calibration standards as well as controls and recoveries are shown in Figures 2 to 5. Typical calibration curves for malathion and malaoxon are shown in Figures 6 and 7.

7.4 GC/MS Confirmation

Use a DB-5 or DB-17 capillary column to achieve separation of samples with malathion and/or malaoxon residues that require confirmation. A gas chromatograph equipped with a mass selective detector can be calibrated to allow detection at 0.05 ppm for both analytes.

7.5 Acceptance Criteria

7.5.1 Retention Time

The retention time of the analytes in the fortified samples and the actual samples should be within ± 0.15 minutes of the retention time of the nearest standard in the analytical set to be accepted as the analyte. This is contingent on the column used and the GC conditions described in this method.

7.5.2 Standard Curve Range

The standard curve range is 0.025 µg/mL to 0.50 µg/mL for both analytes. If a sample peak height exceeds the peak height of the highest standard in the standard curve, then the final extract will be diluted so that its peak height will fall within the standard curve upon reinjection. Evaluate analytes individually for dilutions needed for a given sample.

7.5.3 Recovery From Fortified Samples

Recovery from fortified samples must be in the range of 70% to 120%. Low levels of analyte in the control matrix should be subtracted from the results when calculating recoveries.

7.5.4 Reproducibility

Reproducibility can be measured by results from the validation. Duplicate analyses at a given fortification level should not vary more than 20%.

7.5 Acceptance Criteria (continued)

7.5.5 Peak Shape and Width

Sample peak shape and width are evaluated manually to determine that they are similar to that of the fortified samples.

7.5.6 Calibration Curves

As stated in Section 7.2, the correlation coefficient of the regression line determined for each analyte must be greater than 0.990.

7.5.7 Analysis Time Limits

Samples should be analyzed within 60 days of being homogenized. The final extract should be chromatographed within 7 days after extraction of the homogenized sample.

8.0 CALCULATIONS

8.1 Calculation of ng Found

The ng of analyte found are determined from the standard curve as follows:

$$\text{ng Found} = \frac{\text{Peak height (counts)} - \text{standard curve y intercept (counts)}}{\text{standard curve slope (counts/ng)}}$$

8.2 Calculation of mg-Equivalent Injected

$$\text{mg-equiv injected} = \frac{\text{Sample wt (g)} \times \text{aliquot vol (mL)} \times \mu\text{L inj.} \times 1000\ \text{mg/g}}{\text{Extraction vol (mL)} \times \text{mL final vol} \times \text{dilution factor} \times 1000\ \mu\text{L/mL}}$$

8.0 CALCULATIONS (continued)

8.3 Calculation of ppm Found

$$\text{ppm found} = \frac{\text{ng analyte found}}{\text{mg-equiv injected}}$$

8.4 Calculation of Percent Recovery

$$\%\ \text{Recovery} = \frac{\text{ppm found}^*}{\text{fortification level (ppm)}} \times 100\%$$

* Laboratory fortifications were corrected for any control contribution

8.5 Example Calculation

EL1421-S2, malathion, GC run # 46498, dated 5/21/93, Oranges, Figure 4

Where:

sample weight	= 10 g
aliquot volume	= 100 mL
extraction volume	= 100 mL
µL injected	= 1.0 µL
final volume	= 2.0 mL
peak height (sample)	= 2141 counts
avg. peak height (control)	= 0 counts
y-intercept	= -251.45 counts
slope	= 52677.71 counts/ng
fortification level (ppm)	= 0.01 ppm

$$\text{ng found} = \frac{2141 \text{ counts} - (-251.45 \text{ counts})}{52677.71 \text{ counts/ng}} = 0.0454 \text{ ng}$$

$$\text{mg equiv injected} = \frac{10 \text{ g} \times 100 \text{ mL} \times 1 \text{ µL} \times 1000 \text{ mg/g}}{100 \text{ mL} \times 2.0 \text{ mL} \times 1000 \text{ µL/mL}} = 5.0 \text{ mg}$$

$$\text{ppm Found} = \frac{0.0454 \text{ ng}}{5.0 \text{ mg}} = 0.00908 \text{ ppm}$$

$$\%\ \text{Recovered} = \frac{0.00908 \text{ ppm}}{0.01 \text{ ppm}} \times 100 = 91\%$$

9.0 LIMIT OF QUANTITATION

Adjust the instrument sensitivity, GC calibration standards and final sample volumes to allow detection of malathion and malaoxon at 50% of the LOQ. The LOQ for oranges is 0.01 ppm for each analyte. This is based on the signal to noise ratio being greater than or equal to 5 times baseline noise.

10.0 VALIDATION RESULTS

See Table I for method validation results. The mean and standard deviation for malathion and malaoxon were 84 ± 6.8 (n=10) and 82 ± 9.6 (n=10), respectively.

11.0 REFERENCES

1. American Cyanamid Method M-1886 entitled GC Method for the Determination of Malathion (CL6,601) and Malaoxon (CL28,967) Residues in Alfalfa (Green Forage and Hay) When Using Continuous Automated Sample Injections, issued 3/07/89.

2. EN-CAS Project # 92-0106 entitled Accountability Study of the Proposed Method for the Determination of Malathion (O,O-Dimethyl Phosphorodithioate of Diethyl Mercaptosuccinate) and its Metabolite, Malaoxon, in/on Alfalfa Hay Treated with ^{14}C-Radiolabelled Malathion (MRID # 42894601), issued August 19, 1993

TABLE I

Method Validation Results

The Determination of Malathion and Malaoxon in Whole Oranges

E #	Fort Level (ppm) a	Analyte Fortified	% Recovery Malathion	% Recovery Malaoxon
EL1421-C1	Control	NA	<0 01	<0 01
EL1421-S1	0 01	Both analytes	92	99
EL1421-S2	0 01	Both analytes	91	90
EL1421-S3	0.01	Both analytes	84	79
EL1421-S4	0 05	Both analytes	88	79
EL1421-S5	0.05	Both analytes	80	77
EL1421-S6	0 05	Both analytes	99	88
EL1421-S7	0 50	Both analytes	71	68
EL1421-S8	0 50	Both analytes	89	91
EL1421-S9	0 50	Both analytes	82	72
EL1421-S10	0 50	Malathion only	77	<0 01
EL1421-S11	0 50	Malaoxon only	<0 01	77
		Mean	84	82
		Standard Deviation (n=10)	6 8	9 6

a - The fortification level is expressed as the individual analyte not as parent equivalent.

Table II

Typical Series of Injections Used for the Quantitation of a Set of Samples

Sample	Number of Field Samples
4 standards	
1 control sample	
2 fortified samples, 2 levels	
1 standard	
3 field samples	3
1 standard	
3 field samples	3
1 standard	
3 field samples	3
1 standard	
1 reagent blank	
2 standards	
Total of 23 injections	Total of 9 field samples

NOTE: To prevent possible carryover from samples containing high levels of residues, acetone may be injected following selected samples anticipated by the Principal Analytical Investigator to contain high residues.

FIGURE 1

Flowchart of Analytical Method for Whole Oranges

Determination of Malathion and Malaoxon Residues in Oranges When Using Continuous Autonated Sample Injections

Weigh a 10.0-g sample into an 8-oz. French square bottle

↓

Blend for 2 minutes with 100 mL acetonitrile using an Omni-Mixer homogenizer

↓

Vacuum-filter and rinse with acetonitrile

↓

Partition the sample with 50 mL hexanes (discard hexanes)

↓

Concentrate the extract to 1 - 2 mL using rotary evaporation with a water bath temperature ≤40°C

↓

Add 50 mL acetone + 1.0 g carbon Nuchar C-190N

↓

Vacuum-filter and rinse with 50 mL acetone

↓

Concentrate the extract to incipient dryness using rotary evaporation with a water bath temperature ≤40°C. Dry sample with a gentle stream of nitrogen. Add 1 mL acetone, followed by 9 mL dichloromethane (DCM). Add a small amount of Na_2SO_4 to absorb the water

↓

Pre-condition a Silica Gel Bond Elut with 3 mL 10/90 acetone/DCM, transfer the sample to the bond elut, and collect in a turbovap tube. Rinse the sample flask with 4 mL 10/90 acetone/DCM and collect in the same turbovap tube

↓

Concentrate the sample to dryness using a TurboVap evaporator with a gentle stream of nitrogen and a water bath temperature of 30°C

↓

Add an appropriate volume of 0.02% polyethylene glycol in acetone and vortex for 20 - 30 seconds

↓

Analyze the sample on a GC using a 30-m x 0.32-mm DB-5 capillary column (1.0-um film thickness) and a flame photometric detector (FPD) operating in the phosphorus mode

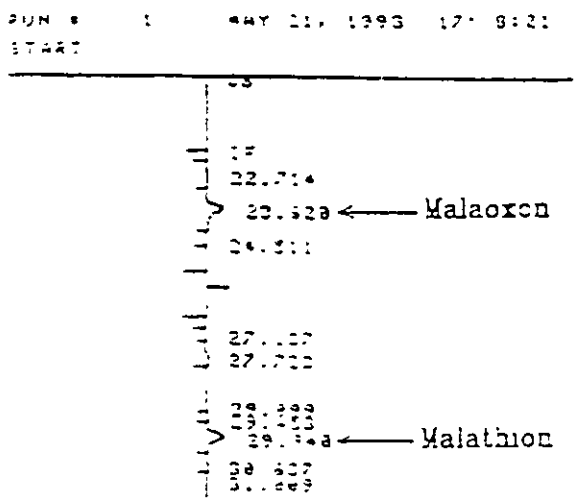
FIGURE 2

Typical Chromatogram

Malathion and Malaoxon

GC Standard

0.025 µg/mL



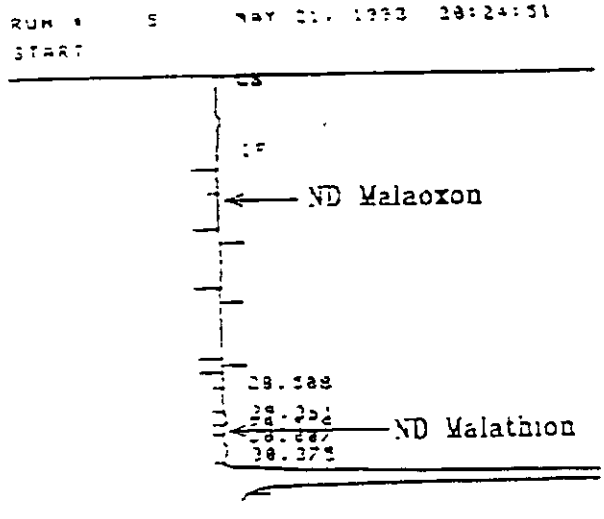
0.025 ng injected
GC run # 46498, set # WW 1, dated 5/21/93

FIGURE 3

Typical Chromatogram

Malathion and Malaoxon

Orange Control



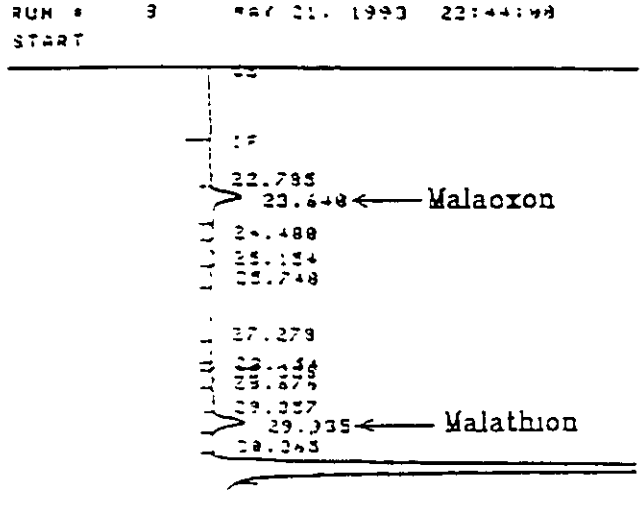
EN-CAS Sample ID #: EL1421-C
Malaoxon ppm Found: <0.01 ppm
Malathion ppm Found: <0.01 ppm
GC run # 46498, set # MV 1, dated 5/21/93

FIGURE 4

Typical Chromatogram

Malathion and Malaoxon

Orange Control + 0.01 ppm
(Malathion and Malaoxon)



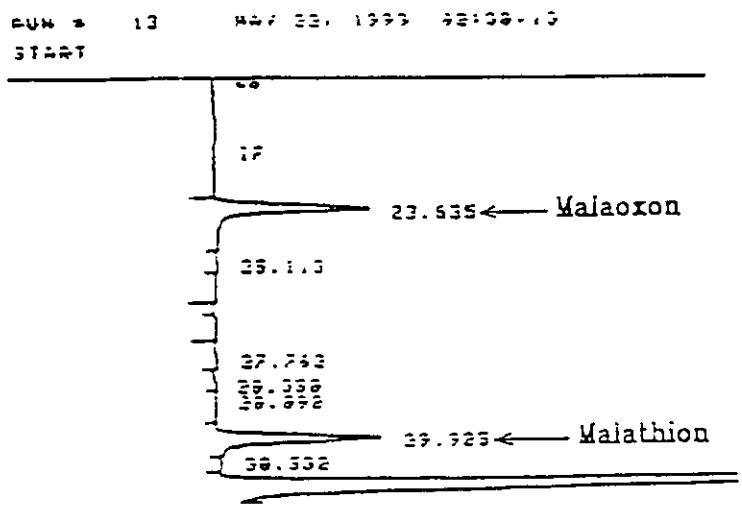
EN-CAS Sample ID #: EL1421-S2
Malaoxon Recovered: 90%
Malathion Recovered: 91%
GC run # 46493, Set # MV 1, dated 5/21/93

FIGURE 5

Typical Chromatogram

Malathion and Malaoxon

Orange Control + 0.05 ppm
(Malathion and Malaoxon)

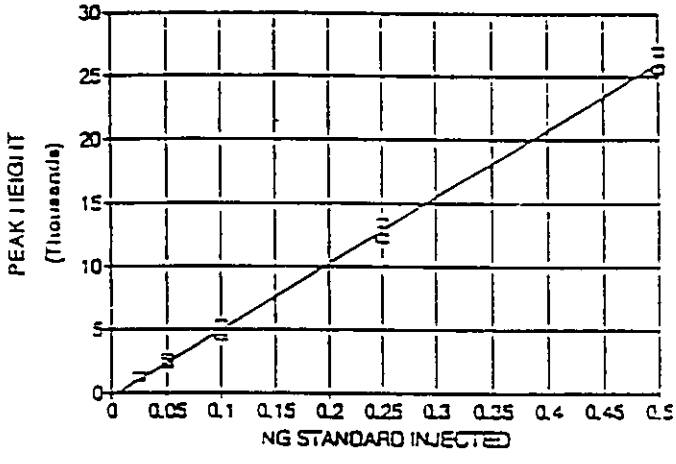


EN-CAS Sample ID #: EL1421-S5
Malaoxon Recovered: 77%
Malathion Recovered: 80%
GC run # 46498, set # MV 1, dated 5/22/93

FIGURE 6

Typical Calibration Curve

Malathion



X	Y
0.025	1254
0.25	12279
0.5	25650
0.05	2308
0.025	1277
0.05	2455
0.1	4912
0.25	12184
0.1	4501
0.5	26565
0.25	13416
0.1	5379
0.05	2666

STATISTICS

Regression Output:

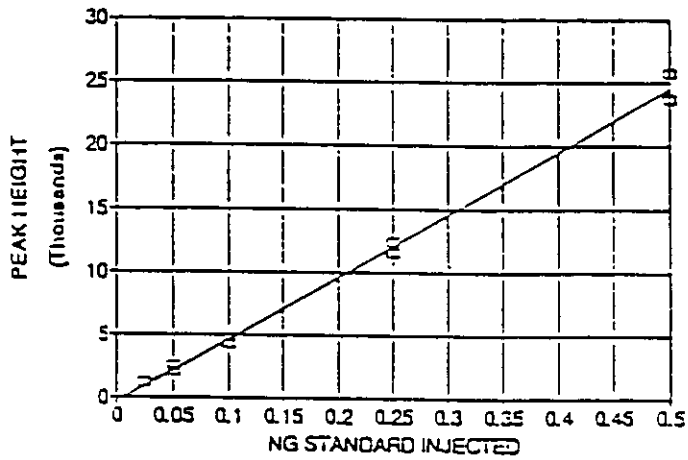
Constant		-251.45	(y-int)
Std Err of Y Est		499.0781	
R Squared		0.997077	(variance)
No. of Observations		13	
Degrees of Freedom		11	
X Coefficient(s)	52677.71		(slope)
Std Err of Coef.	959.3239		
Corr. Coef.	0.998528		

GC run # 46498, set # MV 1, dated 5/21/93

FIGURE 7

Typical Calibration Curve

Malaoxon



X	Y
0.025	1175
0.25	11577
0.5	23705
0.05	2110
0.025	1224
0.05	2477
0.1	4240
0.25	11451
0.1	4361
0.5	25785
0.25	12447
0.1	4802
0.05	2541

STATISTICS

Regression Output:			
Constant		-279.595	(y-int)
Std Err of Y Est		583.1282	
R Squared		0.995501	(variance)
No. of Observations		13	
Degrees of Freedom		11	
X Coefficient(s)	49569.75		(slope)
Std Err of Coef.	1004.756		
Corr. Coef	0.997748		

GC run # 46498, set # MV 1, dated 5/21/93