

Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pesticide Name: Molinate

MRID #: 403917-06

Matrix: Soil

Analysis: GC/ECD

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Appendix D

Method RRC 85-26

Determination of Molinate Residues In Soil
By Capillary Gas Chromatography

C92E100

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DETERMINATION OF MOLINATE RESIDUES IN
SOIL BY CAPILLARY GAS CHROMATOGRAPHY
REPORT NO. 85-25
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Report No. RRC 85-26

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DETERMINATION OF MOLINATE RESIDUES IN SOIL BY CAPILLARY GAS CHROMATOGRAPHY

I. SCOPE

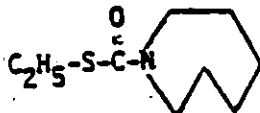
This method is intended for the determination of molinate residues in soil at levels of 0.05 PPM or greater.

II. SUMMARY

A sample of soil is slurried with water and then extracted with toluene. The resulting extract is analyzed directly by capillary gas chromatography with nitrogen-specific detection.

III. INTRODUCTION

Molinate is S-ethyl hexahydro-1-H-azepine-1-carbothioate, the active ingredient in ORDRAM® Selective Herbicide. Molinate has the following structure:





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IV. APPARATUS AND REAGENTS

A. Apparatus

1. Gas Chromatograph. Hewlett-Packard Model 5880A or equivalent, equipped with a nitrogen-phosphorus detector.
2. Gas Chromatographic Capillary Column. Fused silica construction, crosslinked methyl silicone, 12 meter x 0.20 mm i.d., 0.33 μ m coating. Available from Hewlett-Packard.
3. Glass Bottles. Eight-ounce, wide mouth bottles with aluminum foil lined caps; one-ounce, narrow mouth bottles with Poly-seal caps.
4. Syringe. 10 μ L, Hamilton No. 701 or equivalent.
5. Reciprocating Shaker. Eberbach Corporation, model 6010 or equivalent.
6. Centrifuge. IEC International, model C1582 or equivalent.

B. Reagents

1. Solvents. Toluene, Nanograde[®] or equivalent.
2. Sodium Sulfate. Anhydrous, reagent grade.
3. Molinate. Analytical reference-standard molinate. Available from Stauffer Chemical Co., 1200 So. 47th Street, Richmond, CA 94804.
4. Molinate Calibration Solution. Prepare solution containing 50 ng/mL molinate.

V. PROCEDURES

A. Extraction

Weigh 50 g of thoroughly-mixed soil sample into an 8-oz wide mouth bottle. Add 100 mL of distilled water, cap with aluminum foil lined lid and shake on a reciprocating shaker for 30 minutes. Remove cap and add 50 mL toluene. Replace cap and shake for an additional 60 minutes. Centrifuge for 5 minutes at 2,000 RPM to aid separation of the phases. Remove the top (toluene) phase with a disposable pasteur pipet and place in a 1-oz Poly-sealed bottle. Add a layer (approximately 0.5 cm) of sodium sulfate, cap bottle and save for analysis.

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B. Gas Chromatography

Use the following conditions for a Hewlett-Packard 5880 chromatograph equipped with the specified capillary column.

Oven temperature: 90°C for 1 min, then programmed to 160°C at 25°C/min

Detector temperature: 300°C

Carrier flow: 2 mL helium/min

Injection mode: splitless, 220°C

Aliquot injected: 2.0 µL

Retention time: approx. 4.4 min

2. Calibration

Make several injections 2.0 µL of 50 ng/mL calibration solution, to establish a stable response. The HP 5880 data system will record retention times. Either determine peak heights manually or use an on-line data system to record responses.

3. Analysis of Extracts

Inject 2.0 µL of the extracts from the control (untreated soil), fortifications, and treated samples. Measure and record the responses of the peaks coincident in retention time with the peaks produced by the calibration solution injected above. Reinject the calibration solution after every fourth or fifth injection of sample extract, and after all samples have been analyzed, to assure that instrument response is stable. If an extract is found to contain molinate at a detectable level, prepare a response curve using calibration solutions that bracket the estimated concentration range.

VI. CALCULATIONS

A. Calibration Factors

Obtain a calibration factor, F, as follows:

$$F (\text{ng/cm}) = \frac{C \times I}{H}$$

where C = concentration of analyte in calibration solution, ng/µL



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I = volume of calibration solution injected, μL

H = peak height in centimeters.

Alternately, an on-line data system may be used for calibration.

B. Analyte in Sample

With the appropriate calibration factor, F, calculate the concentration of the analyte in the original sample as follows:

$$\text{Concentration (PPM)} = \frac{F \times B}{I \times W}$$

where F = calibration factor, ng/cm

B = peak height from sample extract, cm

I = volume of extract injected, μL

W = mg soil/mL toluene extract.

Preferably, use an average calibration factor from calibration solutions that bracket the samples analyzed.

VII. DISCUSSION

A. Interferences and Clean-up

No clean-up is required when this procedure is utilized as described. However, extractives from soil occasionally contribute peaks with retention times near that of molinate. Satisfactory resolution can usually be achieved with appropriate oven temperature manipulations. Figure 1 shows typical chromatograms.

B. Precision and Accuracy

Controls (untreated soil) and fortifications of these controls should be extracted and analyzed with each set of samples to establish accuracy. Recoveries from 24 samples fortified from 0.05-1 PPM ranged from 80% to 113%, with a mean recovery of 98%. Six injections of a 10 ng/mL standard produced a relative standard deviation of 3%.



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C. Dry Weight Basis

This method determines the residues on an as-received basis. If it is desired to express the values on a dry-weight basis, compensation is necessary for water present in the sample. Percent moisture can be determined by drying a subsample at 105°C for 24 hours.

VIII. REFERENCES

WRC Laboratory Notebook 9661, pages 9-26, 28-31, 43-46.

WRC Laboratory Notebook 9772, pages 6,11.

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IX. SAFETY PRECAUTIONS

A. Toluene

Flammable.

Avoid contact with skin and clothing.

Avoid breathing vapor; work in well ventilated area.

B. Molinate

Avoid contact with skin and clothing.

Work in well ventilated area.

Wash with soap and water after any accidental contact.

Sof1

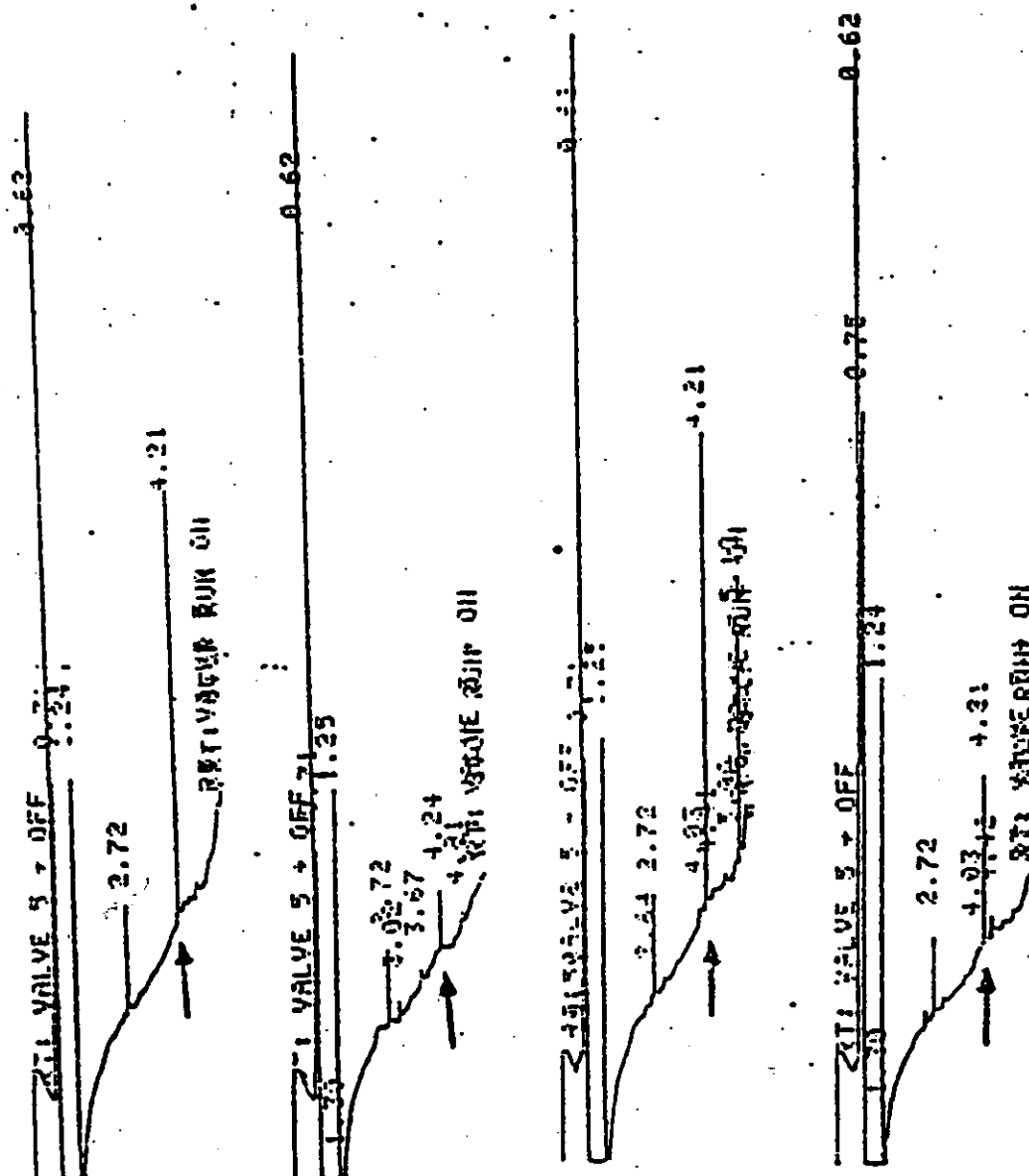


Figure 1. Chromatograms of soil extracts

- a) Standard (50 ng/mL)
- b) Control sample (1 g/mL)
- c) Control fortified at 0.05 ppm (1 g/mL)
- d) Treated sample collected at harvest (1 g/mL)

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