Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Molinate

MRID #: 414218-03

Matrix: Water

Analysis: GC/NPD

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Method No. RRC 85-25 Date 4/22/85

Supersedes _____ Page 1

TITLE: DETERMINATION OF MOLINATE RESIDUES IN WATER BY CAPILLARY GAS CHROMATOGRAPHY

I. SCOPE

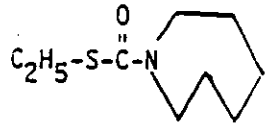
This method is intended for the determination of molinate residues in water at levels of 1 PPB or greater.

II. SUMMARY

A sample of water is extracted with toluene and 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 µm coating. Available from Hewlett-Packard.

3. Glass Bottles. Two-ounce, narrow mouth bottles with Poly-seal caps.

4. Syringe. 10 µL, Hamilton No. 701 or equivalent.

5. Reciprocating Shaker. Eberbach Corporation, model 6010 or equivalent.

6. Ultrasonic Bath. AmericanBrand Ultrasonic Cleaner, model c6450-46 or equivalent.

7. Disposable Pipet. Corning 25 mL disposable pipet or equivalent.

8. Glass Vials. 6-dram vials, with Poly-seal caps, 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 10 ng/mL molinate.

V. PROCEDURES

A. Extraction

Using a disposable 25 mL pipet place a 50 mL subsample in a Poly-seal capped 2-oz bottle. Add 5 mL of toluene. Shake the mixture on a reciprocating shaker for 30 minutes, then sonicate for 1 minute. Remove the upper (toluene) phase by disposable pasteur pipet and place in a clean Poly-seal capped vial. Add a layer (approximately 0.5 cm) of sodium sulfate, cap vial, and save for analysis.

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 of 2.0 µL of 10 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 (deionized water), fortifications, and actual 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:

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

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

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:

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

where F = calibration factor, ng/cm

B = peak height from sample extract, cm

I = volume of extract injected, µL

W = mL water/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 water 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 (deionized water) and fortifications of these controls should be extracted and analyzed with each set of samples to establish accuracy. Recoveries from 70 samples fortified from 1-500 PPB ranged from 88% to 115%, with a mean recovery of 101%. Six injections of a 10 ng/mL standard produced a relative standard deviation of 3%.

VIII. REFERENCES

WRC Laboratory Notebook 9293, pages 1-50.

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.

Water

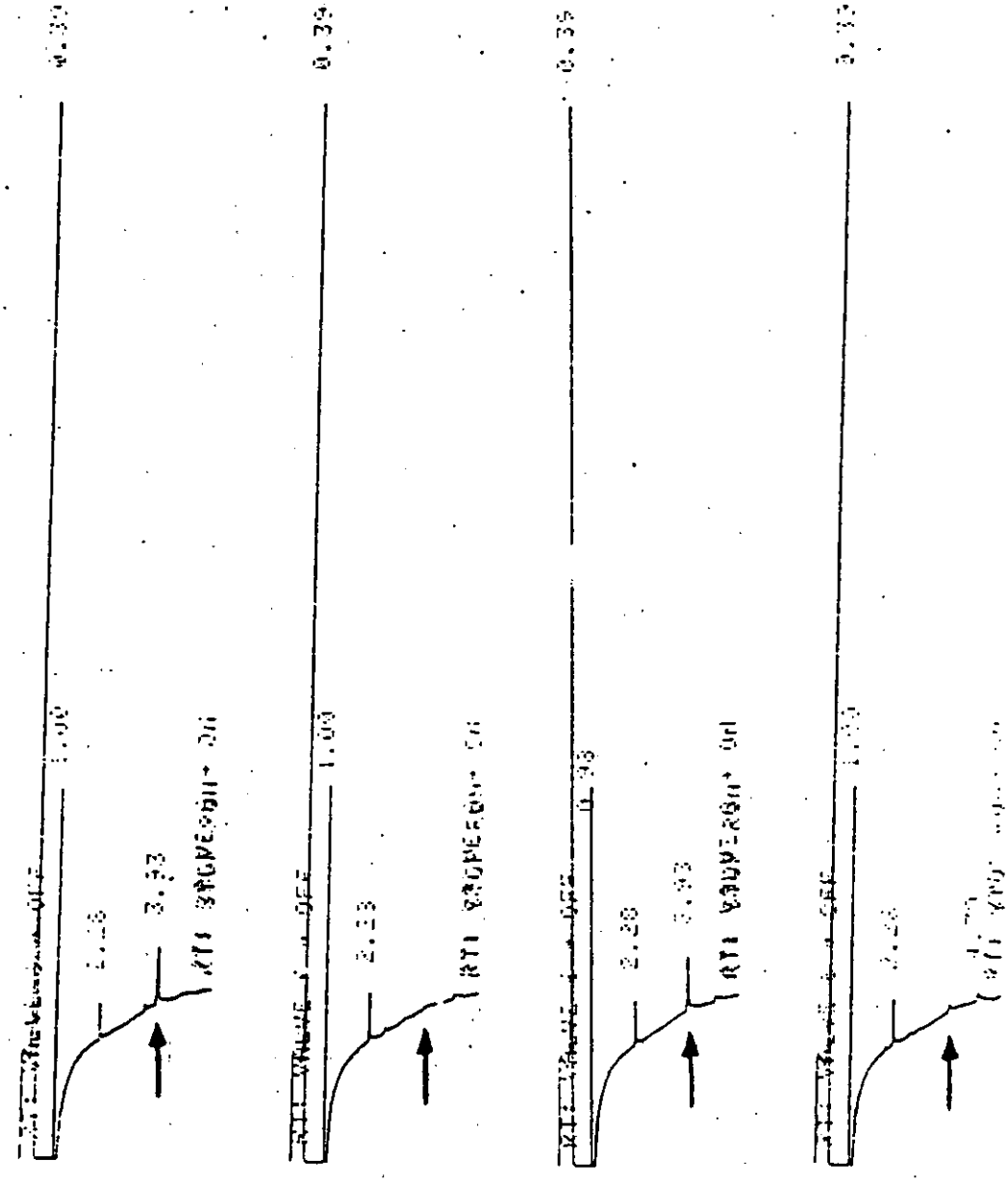

Figure 1. Chromatograms of water extracts

a) Standard (10 ng/mL)
b) Untreated control sample (10 mL/mL)
c) Untreated control fortified @ 2.0 PPB (10 mL/mL)
d) River water from treatment area (10 mL/mL)