



## UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ENVIRONMENTAL CHEMISTRY SECTION  
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JUN 12 1996

MEMORANDUM

SUBJECT: Molinate Method Evaluation in Soil and Water -  
Report No. ECM0096S1/W1

FROM: Aubry E. Dupuy, Jr., Section Chief *Aubry E. Dupuy, Jr.*  
BEAD/ACB/Environmental Chemistry Section

TO: Henry M. Jacoby, Branch Chief  
EFED/Environmental Fate and Groundwater Branch (7507C)

THRU: Donald A. Marlow, Branch Chief *DM*  
BEAD/Analytical Chemistry Branch (7503W)

The EFED/Environmental Fate and Effects Division has requested an Environmental Chemistry Method Evaluation (ECME) on Molinate in soil and water using the Stauffer Chemical Company Methods, "Determination of Molinate Residues in Water by Capillary Gas Chromatography" and "Determination of Molinate Residues in Soil by Capillary Gas Chromatography".

The attached method evaluation report includes three parts:

Part I: Summary and Conclusions

In this section any problems encountered with the method and how they were handled are discussed. ECS's opinion of how well the method performed is also presented.

Part II: Analytical Results

In this section the individual results of each sample at each spiking level for each matrix are listed. The relative standard deviation (RSD) for each spiking level is also presented here.

Part III: Experimental Details

In this section any modification(s) that were made to the method, instrument parameters, spiking levels, explanation of instrument calibration, representative sample and standard chromatograms and standard curves are listed and/or discussed.



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If you have any questions concerning this report, please contact Elizabeth Flynt at (601) 688-2410 or me at (601) 688-3212.

#### Attachments

cc: Danny McDaniel, QA Coordinator  
BEAD/ACB/Environmental Chemistry Section

Elizabeth C. Flynt  
BEAD/ACB/ECS

Environmental Chemistry Method Evaluation Report Number ECM0096W1  
Molinate Determination in Water

Environmental Chemistry Section  
Analytical Chemistry Branch  
Biological and Economic Analysis Division

Prepared by: Elizabeth C. Flynt, Chemist Elizabeth C Flynt 5/30/96  
Signature Date

Reviewed by: Dr. Christian Byrne, QAC Christian Byrne 5/31/96  
Signature Date

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Part I

Summary and Conclusions

We have completed a laboratory evaluation of the Environmental Chemistry Method for the detection of Molinate in water. The method was submitted by Stauffer Chemical Company in accordance with the registration of Molinate (February, 1987).

We feel that this method could be used to monitor water for the presence of Molinate at the levels claimed by the registrant.

No problems were encountered with the extraction procedure, which required little time and only a small amount of solvents, or with the analysis.

The registrant stated the Method Detection Limit (MDL) and the Limit of Quantitation as 0.001 ppm. Therefore, we used the 0.001 ppm level as the MDL and estimated an LOQ to be 0.003 ppm. We extracted fortified water samples at both of the above levels and also at the 10 x LOQ, (0.03 ppm). The precision and accuracy results for all 3 levels were acceptable.

Problems discovered during the method review of the ECM associated with the registration studies for Molinate in water.

- o Chromatograms were only supplied at the MDL, not at the LOQ or above.
- o No explanation of how the Method Detection Limit or Limit of Quantitation was determined.

Problems discovered during the lab evaluation of the ECM associated with the registration studies for Molinate in water.

There were no problems discovered during the lab evaluation of this ECM.

Analytical Results

Method: "Determination of Molinate Residues in Water by  
Capillary Gas Chromatography"

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**Molinate**  
**Fortification Conc. 0.001 ppm = MDL**

<u>Sample</u>	<u>% Recovery</u>
Matrix Blank	ND
Spike 1	120
Spike 2	120
Spike 3	90.0
Spike 4	90.0
Mean Recovery	105
RSD	16.5

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**Molinate**  
**Fortification Conc. 0.003 ppm = LOQ**

<u>Sample</u>	<u>% Recovery</u>
Matrix Blank	ND
Spike 1	100
Spike 2	93.3
Spike 3	103
Spike 4	96.7
Mean Recovery	98.2
RSD	4.26

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**Molinate**  
**Fortification Conc. 0.03 ppm = 10 X LOQ**

<u>Sample</u>	<u>% Recovery</u>
Matrix Blank	ND
Spike 1	90.0
Spike 2	96.7
Spike 3	90.0
Spike 4	103
Mean Recovery	94.9
RSD	6.58

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Part III

Experimental Details

General description of method:

A 50 ml water sample is placed in a 2-oz bottle. Five ml of toluene are added and the bottle capped and shaken on a reciprocating shaker table for 30 minutes, then sonicated for 1 minute. The upper toluene phase is removed by pipette and placed in a clean vial. A layer of sodium sulfate, is added to the vial, which is capped and saved for analysis. The extract is analyzed on a gas chromatograph with a nitrogen phosphorous detector.

Source of analytical reference standards:

- (1) Zeneca Agriculture Products  
Richmond, CA 94804  
Lot No. - ASW01152-01A, Purity - 99.7%

Source of sample matrices:

The water sample was surface water collected at Stennis Space Center on 4/9/96.

Instrumentation for quantitation (listed only if different from that listed in method)

Gas chromatograph: Hewlett Packard(HP) 5890 Gas Chromatograph (GC) equipped with a nitrogen-phosphorous detector.

Instrument for confirmation: Not applicable

Instrument parameters: (listed only if different from that listed in method)

Helium carrier gas: 10 ml/min.

Retention Time: 5.55 minutes

Notes on Analytical Procedure:

*Extraction* - The extraction procedure was very simple and presented no problems.

*Cleanup* - There was no cleanup.

*Analysis* - It was necessary to make one slight modification to

the suggested GC parameters in order to approach the retention time reported by the registrant. The helium carrier gas was set at 10 ml/min. instead of the suggested 2 ml/min. This was necessary in order to shorten the Molinate retention time to 5.3 minutes, which was still longer than the 4.4 minutes reported in the method. The higher gas flow also increased the Molinate response.

### Instrument Calibration

A standard containing Molinate was prepared at the same concentration as the set fortification level and was analyzed either before or after each sample extract. Each extract was measured against the adjacent calibration standard.

### Calculations

The peak area of Molinate in the sample extracts was determined using the GC chromatograms generated from an HP5890 GC.

sample area	concentration	final volume			
counts	of std.in(µg/ml)	of sample extract (ml)	X 1ml water	=residue	
std. area	X Molinate	X original volume of sample (ml)	1g water	in	
counts	X			sample	(ppm)

The percent recovery was calculated as follows:

$$\frac{\text{amount of residue detected in sample (ppm)}}{\text{amount of residue initially added to sample (ppm)}} \times 100\% = \text{percent recovery}$$

### Example:

**Spike 2**  
**0.003 ppm Fortification Level**

$$\frac{2863}{3071} \times \frac{.03\mu\text{g/ml}}{50 \text{ ml}} \times \frac{5\text{ml}}{1\text{ml/g}} = 0.0028 \text{ ppm recovered}$$
$$\frac{0.0028 \text{ ppm}}{0.003 \text{ ppm}} \times 100 = 93.3\% \text{ recovery}$$



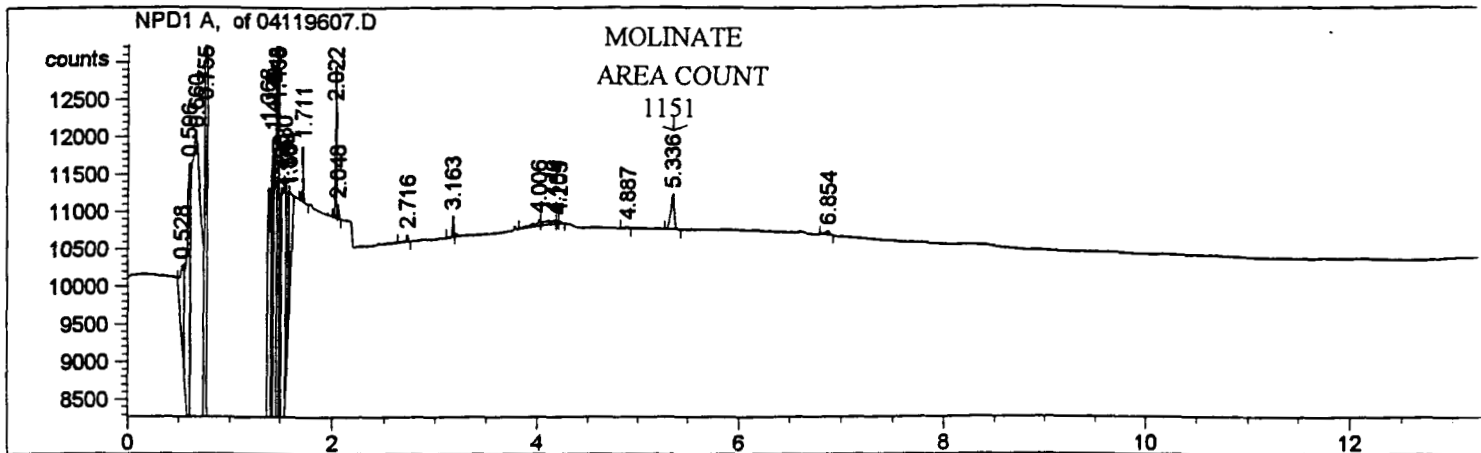
**Chromatograms and Calibration Curves:**

**Molinate**

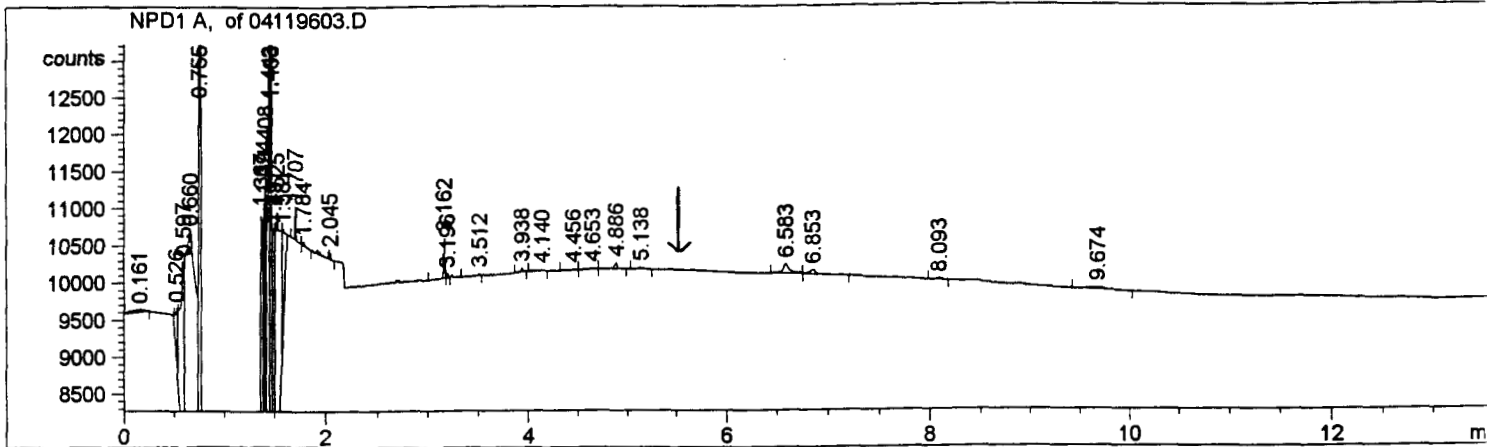
- A. GC Chromatograms at the 0.001 ppm Fortification Level
  - A-1. 2 $\mu$ l @ 0.01  $\mu$ g/ml (equiv. to 0.001 ppm) Calibration Standard
  - A-2. Water Matrix Blank for 0.001 ppm level
  - A-3. Water Fortified at 0.001 ppm
  
- B. GC Chromatograms at the 0.003 ppm Fortification Level
  - B-1. 2 $\mu$ l @ 0.03  $\mu$ g/ml (equiv. to 0.003 ppm) Calibration Standard
  - B-2. Water Matrix Blank for 0.003 ppm level
  - B-3. Water Fortified at 0.003 ppm
  
- C. GC Chromatograms at the 0.03 ppm Fortification Level
  - C-1. 2 $\mu$ l @ 0.3  $\mu$ g/ml (equiv. to 0.03 ppm) Calibration Standard
  - C-2. Water Matrix Blank for 0.03 ppm level
  - C-3. Water Fortified at 0.03 ppm
  
- D. Standard Linear Regression Curve

# A. Molinate GC Chromatograms at the 0.001 ppm Fortification Level

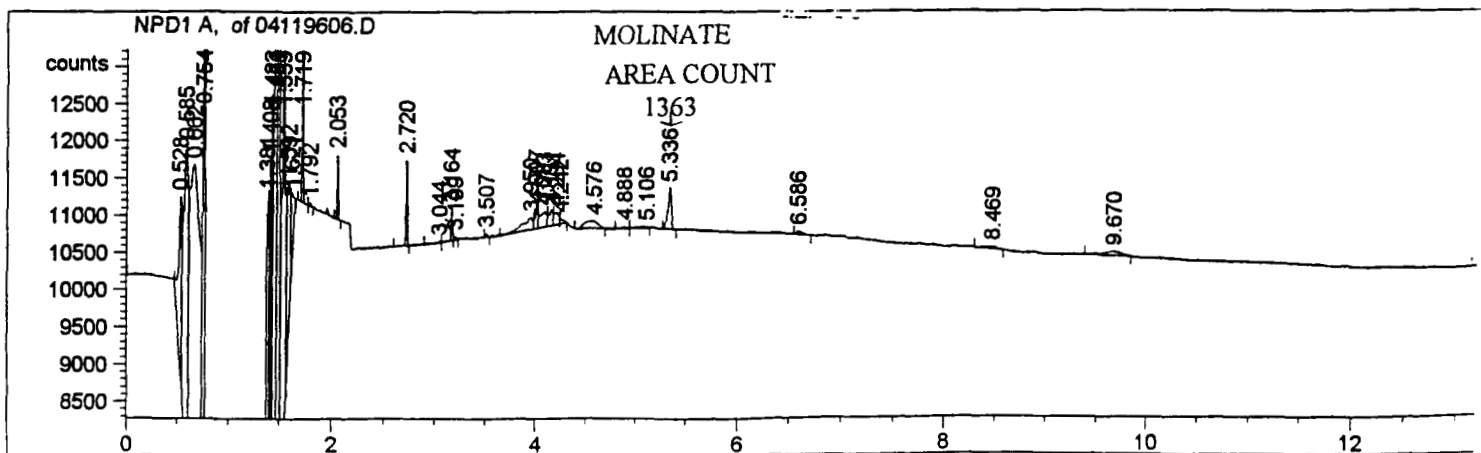
A-1. 2  $\mu$ l @ 0.001 ug/ml (equiv. to 0.001 ppm) Molinate Calibration Standard



A-2. Water Matrix Blank for 0.001 ppm level

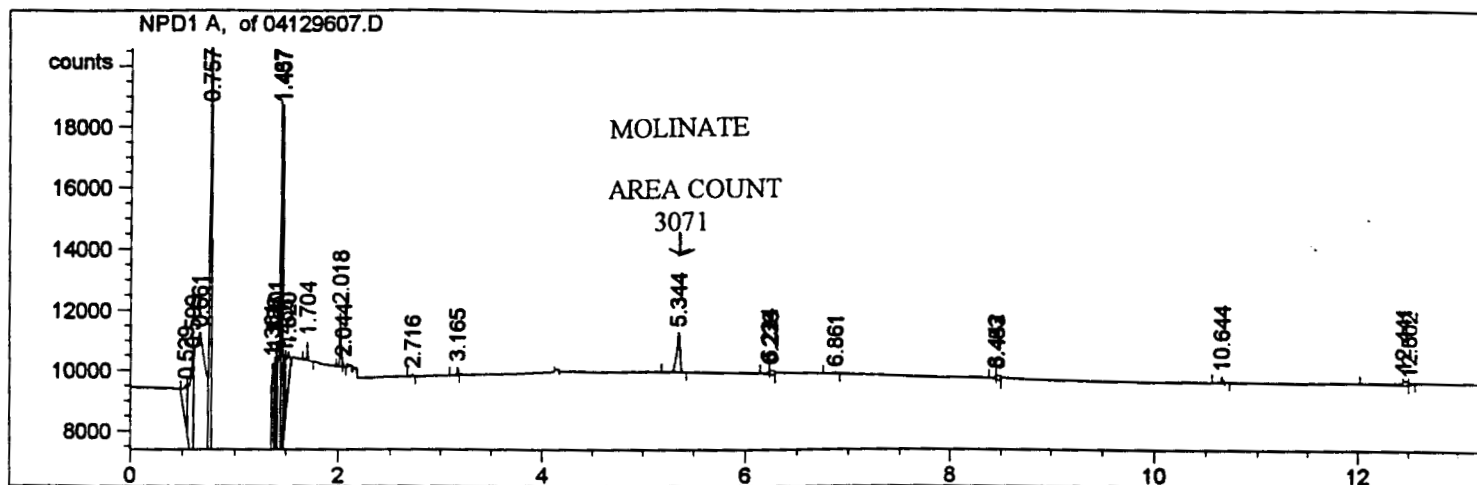


A-3. Water Fortified at 0.001 ppm

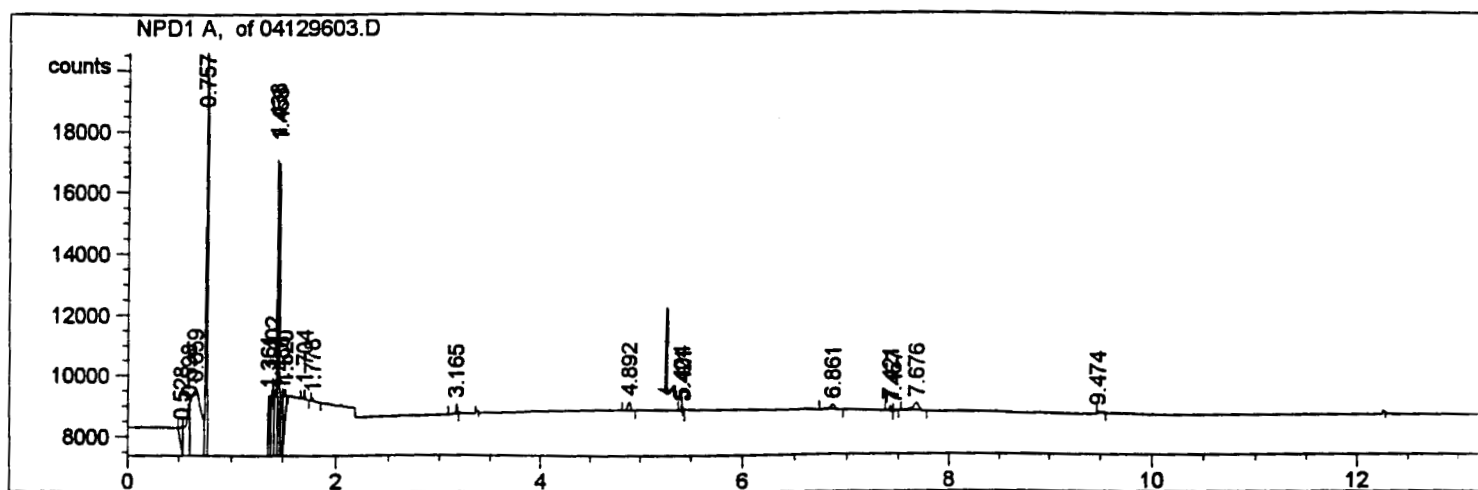


## B. Molinate GC Chromatograms at the 0.003 ppm Fortification Level

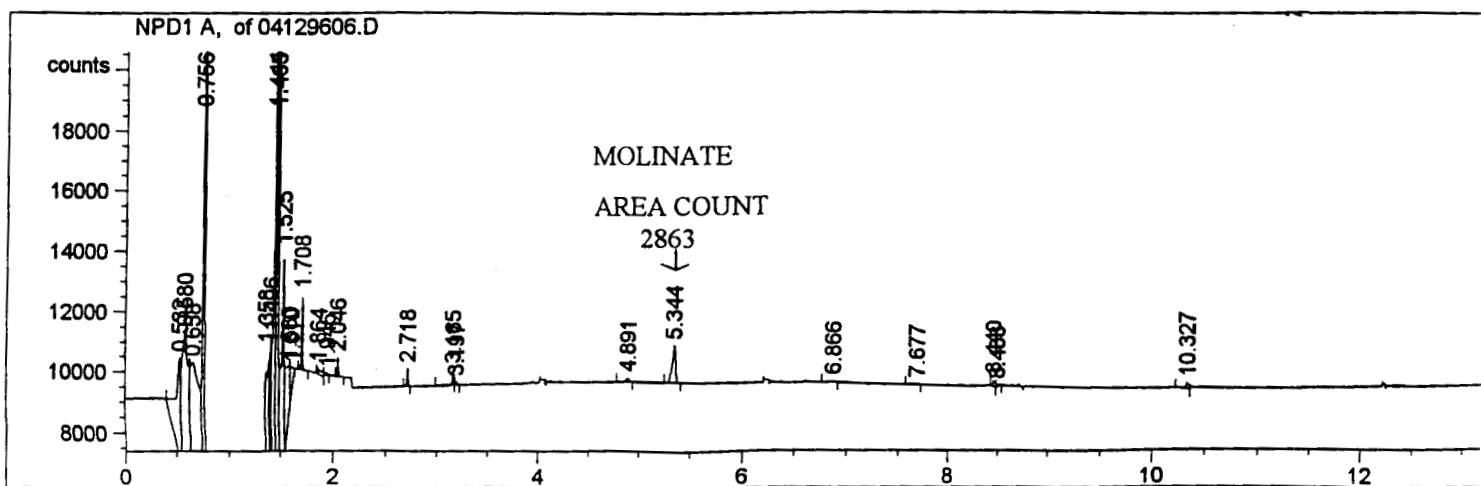
B-1. 2  $\mu$ l @ 0.003 ug/ml (equiv. to 0.003 ppm) Molinate Calibration Standard



B-2. Water Matrix Blank for 0.003 ppm level

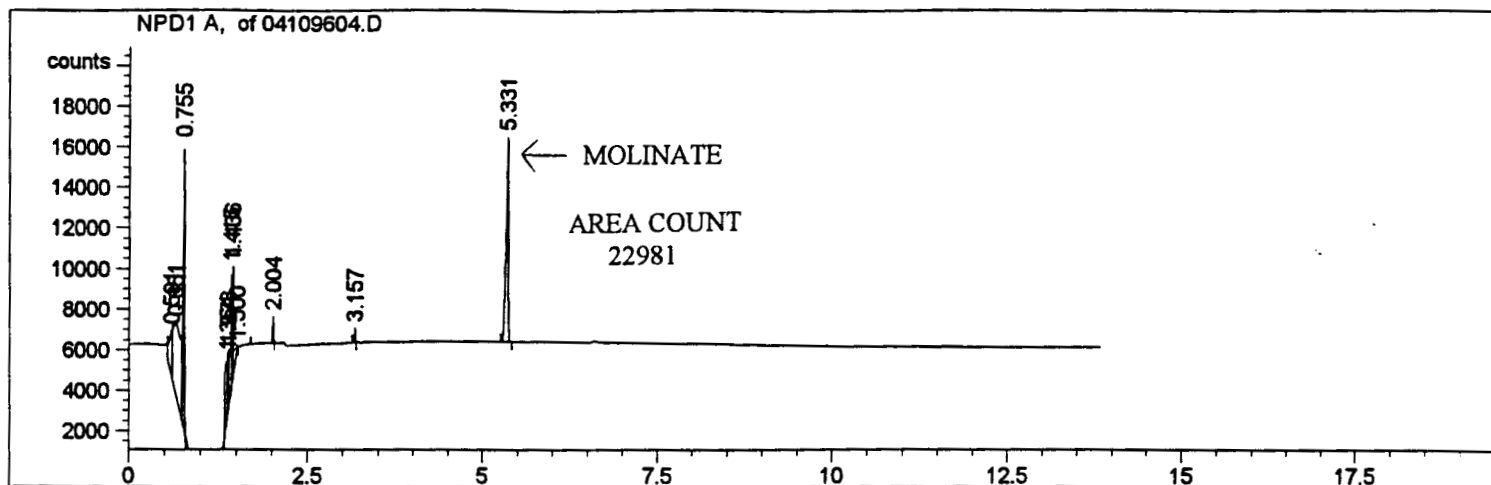


B-3. Water Fortified at 0.003 ppm

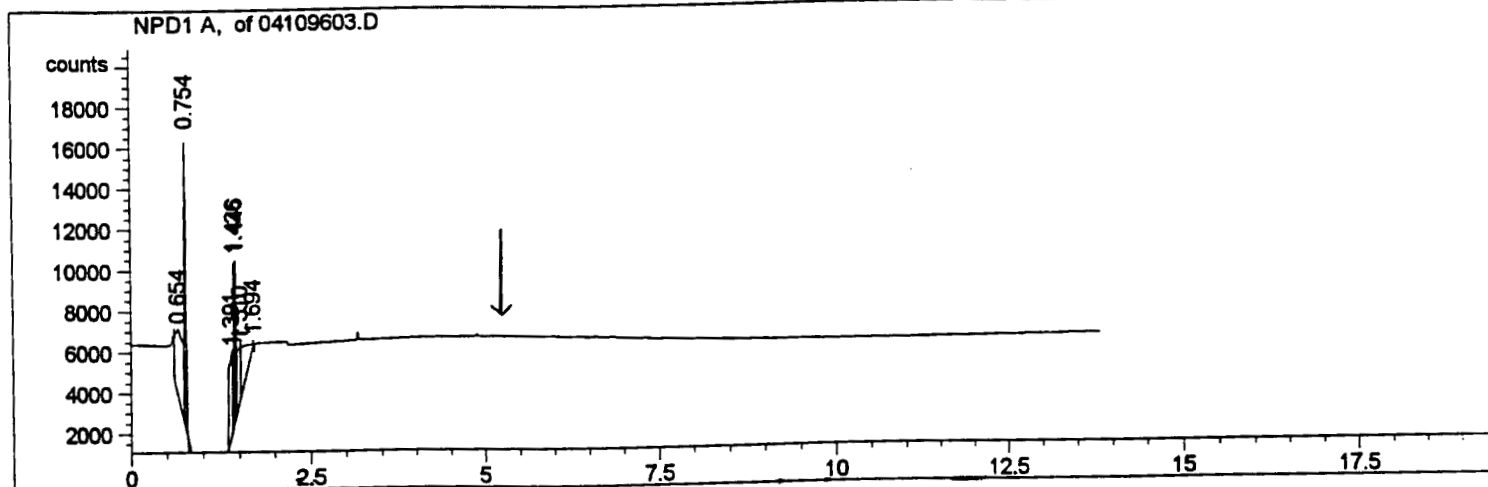


## C. Molinate GC Chromatograms at the 0.03 ppm Fortification Level

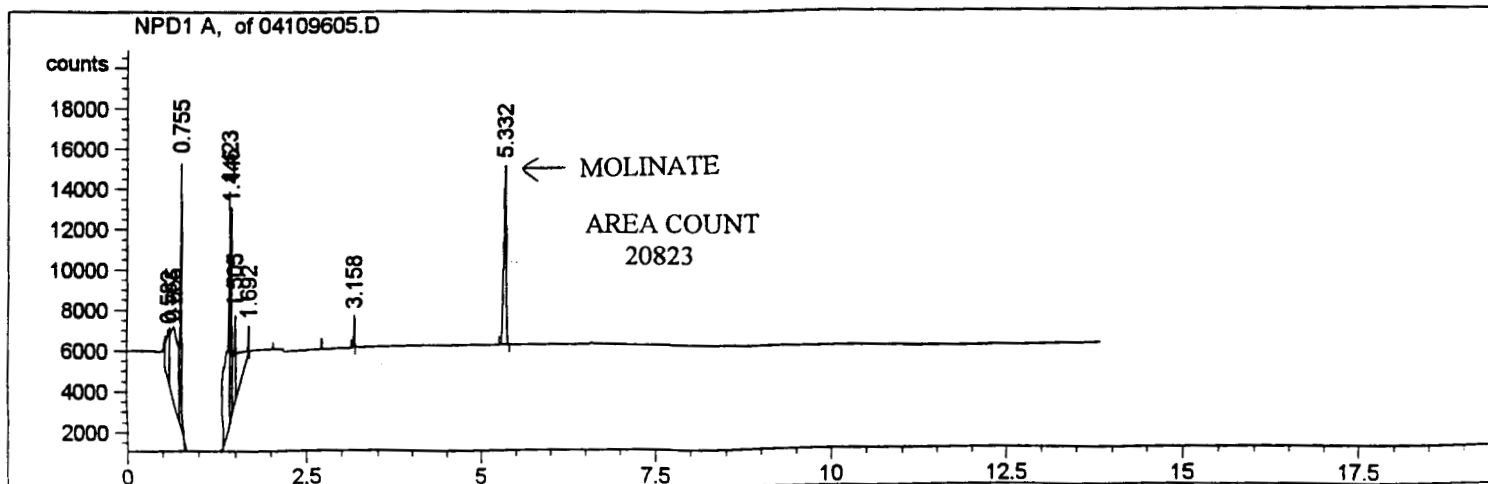
### C-1. 2 $\mu$ l @ 0.03 ug/ml (equiv. to 0.03 ppm) Molinate Calibration Standard



### C-2. Water Matrix Blank for 0.03 ppm level



### C-3. Water Fortified at 0.03 ppm



# D. Molinate Standard Linear Regression

Inject Volume: 2  $\mu$ l

(Range includes 0.001 ppm through 0.5 ppm)

ECM0096W1

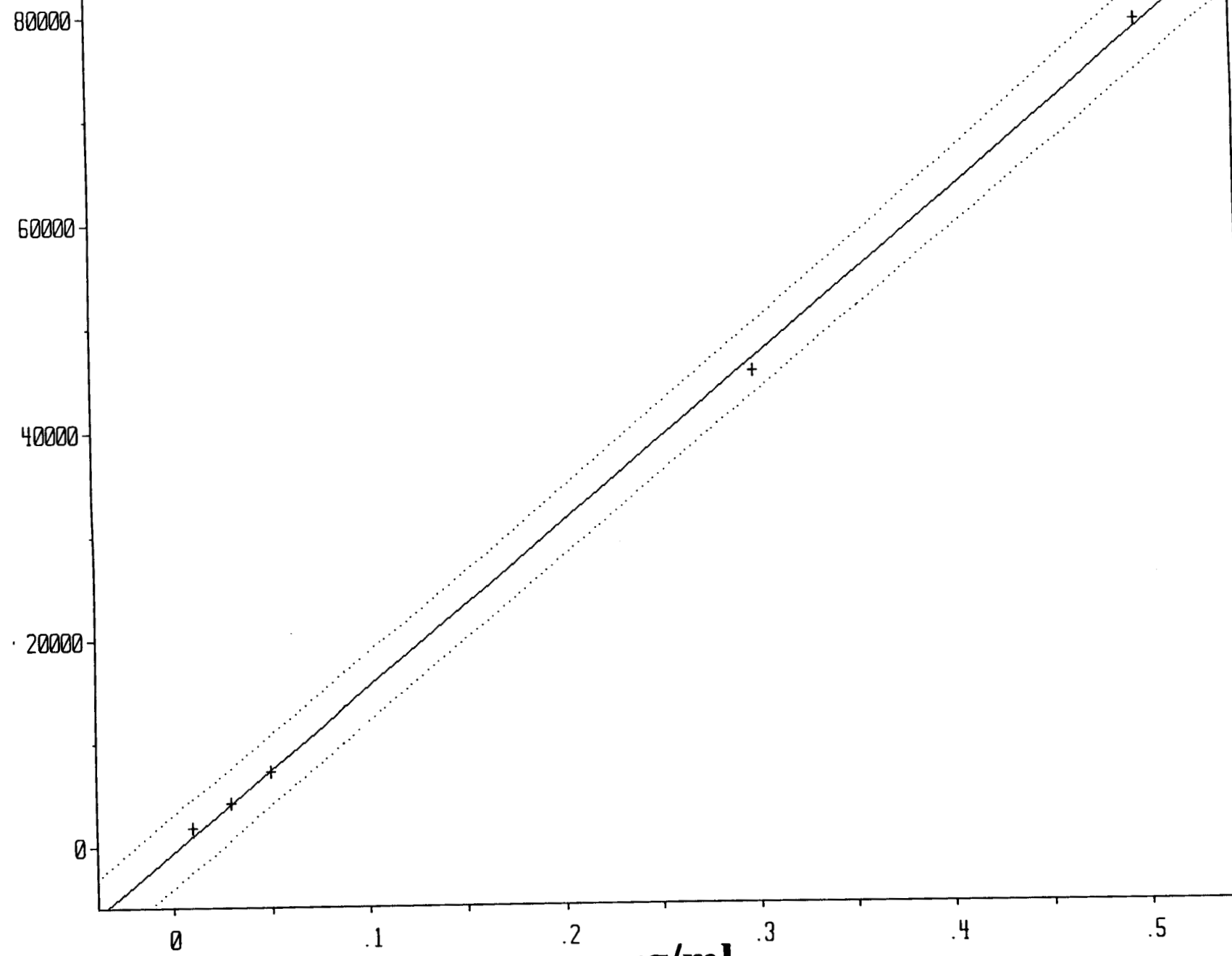
05/24/96

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## Molinate Standard Linear Curve

Area Predicted By Concentration

AREA  
COUNTS



Linear:  $Y = -490.6582 + 157368.9 * X$   $\mu$ g/ml

Correlation Coefficient = 0.9997

Linear —  
95% C.I. ....

## Appendix A:

### Molinate Chemical Structure

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

