Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Quinclorac

MRID #: 410635-68

Matrix: Soil

Analysis: GC/MS

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THE DETERMINATION OF QUINCLORAC (BAS 514 H) AND ITS METABOLITE (BH 514-1) RESIDUES IN SOILS BY GC/MS TECHNIQUES

Method No. A8901

Date Issued: February 1989

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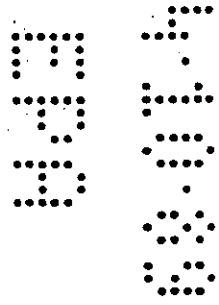

QUALITY ASSURANCE STATEMENT

The procedures described and the results reported herein are correct and accurate, to the best of our knowledge.

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1 INTRODUCTION AND SUMMARY

1.1 Scope and Source of Method

1.1.1 Scope

Quinclorac (BAS 514 H) is an experimental herbicide being developed by BASF Corporation for use in rice and turf. It is currently being formulated as a 50% wettable powder. It is generally applied pre or post emergence to rice at 0.5 lb ai/A either under flooded or nonflooded conditions to control barnyard grass and certain broadleaf weeds. For turf, BAS 514 H is applied post emergence at 1 lb ai/A to control certain broad leaf weeds and crabgrass. Quinclorac, 3,7-dichloro-8-quinoline-carboxylic acid, is metabolized by dechlorination to 3-chloro-8-quinoline-carboxylic acid (BH 514-1). The analytical method was developed to measure both BAS 514 H and BH 514-1 in turf and aquatic soils.

1.1.2 Source

This method was developed by Dr. Victor Winkler at the Agricultural Research Center in Research Triangle Park, N.C. to measure quinclorac residues in a confined field dissipation study (Protocol M8813).

1.1.3 Principle of Method

The residues are extracted by refluxing in dilute alkali and partitioned into ethyl acetate at pH 1. The residues are derivatized to methyl esters using diazomethane and purified by preparative TLC. Total sample work up time is about 4 hours. The lower limit of quantitation ranges between 0.01 and 0.05 ppm depending upon the soil type and equipment.

1.1.4 Validation Studies

1.1.4.1 BASF

The mean ± standard error % recovery for a validation conducted by BASF on three aquatic soils (CA, TX; MS) spiked at three concentrations of 0.010, 0.055, 0.113 ppm was 100% ± 7.7 and 95% ± 18.8 for ^{14}C-BAS 514 H and BH 514-1 (n = 18), respectively.

1.1.4.2 CompuChem

A second set of validation samples were prepared by BASF and analyzed by CompuChem Laboratory (an independent contract laboratory). These results were nearly identical to the first validation study showing no significant differences between soil type, spike level or compound. The same extracts for the 0.05 ppm spikes were analyzed at both labs. There was also very good agreement between CompuChem and BASF with the following recoveries (BASF vs CompuChem): % BAS 514 H, 108 vs 119; % BH 514-1, 108 vs 104. From these results it is concluded that Method A8901 is valid for the determination of BAS 514 and BH 514-1 residues in soil.

2 MATERIALS AND METHOD

2.1 Equipment

- Erlenmeyer flasks with standard ground joint: 500 mL
- Volumetric pipettes: 1 mL; 2 mL; 10 mL
- Round bottom flasks: 250 mL
- Graduated cylinders: 100 mL
- Powder funnels: 10 cm
- Separatory funnels: 250 mL
- Snyder column (conderser): 3 ball
- Stirrer hot plates: standard
- Magnetized stir bars: standard
- Rotary evaporator: standard
- TLC developing chamber: 20 x 20 plates
- Balances: analytical and top load
- Gas Chromatograph and mass spectrometer: Varian Model 3300, or equivalent, interfaced into Nermag P-10-10 Mass Spectrometer, or equivalent, and a 5 m x 0.25 mm DB-5 column (J&W, Inc.). Operating conditions: Temperatures (°C) - Column, 100 to 240 @ 50/min and isothermal for 3 min to clean column; injection 230, flow 2 mL/min helium; SIM at m/z 190 (BH 514-1 ME) and 224 (BAS 514 H); integration time at 100 milliseconds.
- Tenivent vector 2 data system, or equivalent.
- Sliding needle injector, Chrompack Model 8992, or equivalent (optional for microsyringe injection).
- Centrifuge Beckman Model J-21C equipped with J-14 rotor, or equivalent.

2.2 Reagents and Chemicals

Solvents must be pesticide grade or equivalent. Suitable products are available from Burdick and Jackson Laboratories, Inc., and other manufacturers.

- Ether, anhydrous
- Ethyl acetate (distilled in glass)
- Methanol
- Hexane
- Carbitol
- Potassium hydroxide solution, 60% v/w in water
- Sodium hydroxide solution, 0.1 N in water
- Hydrochloric acid solution, 1 N in water
- Acetic acid solution, 10% water
- Sodium Sulfate, anhydrous
- N-methyl-N-nitroso-p-toluenesulfonamide (Diazald™, Aldrich Chemical Co.)
- Universal pH indicator sticks, pH 0-14
- Cotton or glass wool
- TLC Plates: 20 x 20 cm, 250 μm Silica gel 60 with a pre-adsorbent strip (Whatman LK6F)
- Microfilters compatible with methanol: 0.45 μm (Acrodisk CR®, Gelman Sciences)
- Syringes: 5 mL to fit microfilters (Scientific Products)

2.2.1 Preparation of Diazomethane Solution

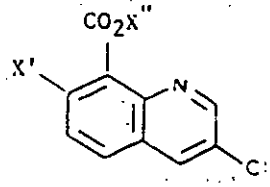
Preparation of diazomethane solution (in a hood): Add a few milliliters of diethyl ether to test tube A. Add 50 mL of diethyl ether and 12.5 mL of methanol to a 100 mL screw cap volumetric flask. Add 2.0 mL of carbitol, 2.0 g of diazald, and 2.0 mL of diethyl ether to test tube B. Use the ether solution to rinse the walls of the test tube. Slowly bubble nitrogen into the solution in test tube A, from test tube A into the solution in test tube B, and from test tube B into the solution in the volumetric flask. Allow gas to escape from the volumetric flask into a 10% acetic acid trap. Continue bubbling nitrogen until the yellow color in test tube B dissipates and a deep yellow color forms in the solution in the volumetric flask. The level of diazomethane in the volumetric flask is adequate for the set of 8 samples. Quench any remaining diazomethane solution in test tube B with 10% acetic acid. The yellow color will disappear.

2.3 Standard Substances and Solutions

2.3.1 Standards

- 3,7-dichloro-8-carboxylic acid (BAS 514 H) standard: 99+% pure (BASF, Limburgerhof, FRG)
- 3-chloro-8-carboxylic acid (BAS 514-1) standard: 99+% pure (BASF, Limburgerhof, FRG)
- 3,7-dichloro-8-carboxylic acid methyl ester (BAS 514 ME): 99+% pure (BASF, Limburgerhof, FRG)
- 3-chloro-8-carboxylic acid methyl ester (BH 514-1 ME): 99+% pure (BASF, Limburgerhof, FRG)

2.3.2 Structures



	X'	X"
BAS 514 H	-Cl	-H
BH 514-1	-H	-H
BAS 514 ME	-Cl	$-CH_3$
BH 514-1 ME	-H	$-CH_3$

2.3.3 Preparation of Solutions

(a) BAS 514 H stock solution: 1 mg/mL. Dissolve 50 mg BAS 514 H in methanol and dilute to 50 mL with same solvent.

b) BH 514-1 stock solution: 1 mg/mL. Same as above, using BH 514-1.

(c) BAS 514 ME stock solution: 1 mg/mL. Same as above, using BAS 514 ME.

(d) BH 514-1 ME stock solution: 1 mg/mL. Same as above, using BH 514-1 ME.

(e) BAS 514 H plus BH 514-1 working solution A: 10 mcg/mL admixture. Mix 1 mL each of (a) BAS 514 H and (b) BH 514-1 1 mg/mL stock solutions and dilute to 100 mL with methanol.

(f) BAS 514 H plus BH 514-1 spiking solution: 1 mcg/mL admixture. Dilute 10 mL (e) working solution A to 100 mL with methanol.

(g) BAS 514 ME plus BH 514-1 ME working solution B: 10 mcg/mL admixture. Mix 1 mL each of (c) BAS 514 ME and (d) BH 514-1 ME 1 mg/mL stock solution to 100 mL with methanol.

(h) BAS 514 ME plus BH 514-1 ME working solution C: 1 mcg/mL admixture. Dilute 10 mL (g) working solution B to 100 mL with methanol.

(i) BAS 514 ME plus BH 514-1 ME standard solution A: 100 ng/mL admixture. Dilute 10 mL (h) working solution C to 100 mL with methanol.

(j) BAS 514 ME plus BH 514-1 ME standard solution B: 50 ng/mL admixture. Dilute 5 mL (h) working solution C to 100 mL with methanol.

(k) BAS 514 ME plus BH 514-1 ME standard solution C: 5 ng/mL (5 pg/mcL) admixture. Dilute 10 mL (j) standard solution B to 100 mL with methanol.

2.3.4 Stability of Standard Solutions (BASF Residue No. 266)

Storage days	Room Temperature Daylight	4°C Refrigerator
	(3,7-Dichloro-8-quinolinecarboxylic acid methyl ester 2) 0.2 g/mL in acetone	
7	99.7%	103.8%
35	100.1%	100.8%
106	-	101.1%

2.3.5 Preparation of Standard Curves

The following standard curve solutions are prepared to cover a soil residue range of 0.025 to 0.10 ppm for final equivalent sample concentrations of 0.5 g/mL. The lowest standard curve concentration should be at 50% of the lowest spiked control

sample used for recovery analysis. If the soil sample matrix causes peak enhancement than standard curves solutions must be prepared using 1:1 v/v admixtures of standard solutions and control soil extracts.

2.3.5.1 Sliding Needle Technique

To calibrate the GC/MS using a sliding needle injection technique various aliquots are taken from the standard solution C and applied to the injection needle as shown below.

Standard Solution C @ 5 pg/mcL	pg/Injection
2.5 mcL	12.5
5 mcL	25
10 mcL	50

2.3.5.2 Microsyringe Technique

To calibrate the GC/MS using a microsyringe technique prepare the following standard curve solutions by diluting the 1 mcg/mL working solution C with methanol as shown below:

Std. Curve Solution No.	Working Sol. C mL @ 1 mcg/mL	Methanol mL Dilution	pg/1 mcL Injection
1	1.25	98.75	12.5
2	2.5	97.5	25
3	5.0	95.0	50

3 ANALYTICAL PROCEDURE

3.1 Preparation of Sample

(1) Soil cores are sectioned into predesignated lengths (defined by study protocol).

(2) Replicate sections are air dried to a consistency which is suitable for pulverizing (typically between 2 and 8% moisture)

(3) The air dried soil cores are pulverized either by milling or by mortar and pestle to approximately 10 mesh and mixed thoroughly before sampling for analysis.

(4) Aliquots of the soil samples are assayed for moisture content either by loss-on-oven drying or Karl Fisher techniques.

3.2 Extraction of Sample

(1) Each sample is assigned a discrete identification number with each extraction which stays with it throughout the analysis and is included with the final analytical result.

(2) Each soil sample of known weight (20 g) is refluxed in 0.1 N NaOH (200 mL) for one hour and allowed to settle. Control Soils are spiked to 0.01, 0.05 and 0.10 ppm by adding 0.2, 1 and 2 mL of the spiking solution (f) for each analytical batch.

(3) Sufficient solution is centrifuged at a speed to obtain a known aliquot (50 mL) of moderate clarity (e.g., 5,000 rpm x 10 min).

(4) The aliquot (50 mL) is acidified to ca pH 1 with 1 N HCl and extracted 3 times with an equivalent volume of ethyl acetate (3x30 mL). Methanol can be used to break emulsions.

(5) Each ethyl acetate extract is passed through anhydrous Na_2SO_4 into a 250 mL R.B. flask which is followed by a final ethyl acetate wash (25 mL) of the Na_2SO_4.

(6) The ethyl acetate extract is taken just to dryness by rotary evaporation at 45°C and reacted in a hood with 10 mL of fresh dark yellow diazomethane solution in ether:methanol (8:2) for 30 min to 1 hour. If solution does not remain yellow, add more diazomethane.

(7) The reaction mixture is taken just to dryness by rotary evaporation at 45°C and resuspended in 2 mL methanol. Excessive drying of the methyl ester derivatives may result in sublimination and cause low recoveries.

(8) A 1 mL aliquot of the resuspended residue is pipetted onto the preabsorbant zone of a 20x20 Whatman LK6F 250 micron TLC plate. Hot air drying between passes is optional.

(9) The plate has ca a 2 cm runway scored on one side for developing ca 5 mcg of the methyl ester reference standards, BAS 514 ME and BH 514-1 ME. Use a mixture (1:1 v/v) of the 1 mg/mL stock solutions (c) and (d).

(10) The TLC plate is developed to 10 cm with hexane:ethyl acetate (1:1) and allowed to air dry.

(11) The sample residue zone is located under 254 nm UV light using the BAS 514 ME and BH 514-1 ME spots as the upper and lower reference points (A typical developed TLC plate is shown in Figure 1).

(12) The sample residue zone (ca 2 cm) is scraped off the plate and transferred into vials containing a known volume of MeOH (5 mL).

(13) The sample is mixed (ca 15 seconds) and an aliquot (ca 2 mL) is withdrawn into a 5 mL syringe and filtered through a 0.45 micron filter (Acrodisk™) to clarify the solution for GC/MS(SIM) analysis.

(14) Weights and volumes taken for the total process are recorded for each sample to obtain equivalent sample weights as shown in the example below:

$$\frac{20\text{ g sample}}{200\text{ mL (alk ext.)}} \times \frac{50\text{ mL (partition aliquot)}}{2\text{ mL (MeOH resuspension)}}$$

$$\times \frac{1\text{ mL (MeOH for TLC)}}{5\text{ mL (MeOH resuspension)}}$$

= 0.5 g equivalent sample wt per mL in the final solution.

(15) If necessary dilute samples with methanol to keep peak responses within the standard curve range.

3.3 Instrumentation

3.3.1 Description

Location of Use	BASF	CompuChem
Gas Chromatograph	Varian 3300	Perkin Elmer Sigma 3B
Mass Spectrometer	Nermag P-10-10	Finnigan OWA
Capillary Column	DB5; 5m x 0.05mm	DB5; 20m x 0.32mm thick film
Injection Technique	Sliding Needle	Microsyringe

3.3.2 Operating Conditions

Location of Use	BASF	CompuChem
Injection Temp	230°C	250°C
Oven Temperature	100°C to 240°C @ 50°C/min	130°C to 310°C at 18°/min
Retention Time		
BAS 514 ME	1.8 min	8.3 min
BH 514-1	1.5 min	7.3 min
Carrier Gas	He @ 2 mL/min	He @ 1 mL/min
Injection Volume	1 mcL	3 mcL
Internal Standard	none	0.5 pg/mcL D_{10} Phenanthrene and D_{10} Acenaphthene

3.3.3 Calibration Procedures

The GC/MS conditions are adjusted to give a response for the lower limit of quantitation to be ca 10 times background. This is typically in the 5 to 25 pg range, which is at 0.01 to 0.05 ppm residue levels for a 0.5 mg/mL sample equivalent weight final solution. Typically, the strongest ions for monitoring are m/z 224 for BAS 514 H ME and m/z 190 for BH 514-1 ME.

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Standard curves are prepared by plotting peak area as the independent variable versus pg standard injected as the dependent variable. Linearity and zero y-intercept response must be established prior to conducting sample analysis if calculations are to be done by proportionality equations. If there is a peak response enhancement by a sample matrix effect, then the standard curve solutions must be prepared using 1:1 v/v admixtures of standard solutions and control soil extracts.

If linearity can not be established (i.e., coef corr, $R \geq 0.95$), then a nonlinear but consistent standard curve must be established (i.e., relative std dev, $CV \leq 10\%$).

3.4 Sample Analysis

After linearity (or at least a consistent standard curve response) has been established by injecting various amounts of standard solution, (e.g., 12.5, 25 and 50 pg BAS 514 ME + BH 514-1 ME) and graphing the corresponding integrated counts, known amounts of samples are injected and the BAS 514 ME and BH 514-1 ME peak response recorded. If necessary more or less sample material is injected for peak responses to correspond to the range of the standard curves. The calibrations must be checked by injecting a reference standard at least between every 10 samples or every twelve hours, whichever comes first. If the calibration has change all analysis following the previous calibration are invalid.

3.5 Interferences

3.5.1 Sample Matrices

If interfering peaks occurs at m/z 190 for BH 514-1 ME or m/z 224 for BAS 514 H ME reassay using alternative ions (See Figure 2).

3.5.2 Other Pesticides

None known to date.

3.5.3 Solvents

None known to date.

3.5.4 Labware

None known to date.

3.6 Confirmatory Techniques

Multiple ion peak matching:

3.7 Time Required for Analysis

The time required for a set of 6 samples, 2 recoveries and 1 control is about 8 hours. This includes sample preparation GC/MS analysis and the data report provided that no special problems arise.

3.8 Potential Problems

Low recoveries can possibly result from sublimination of the methyl ester derivatives if rotary evaporation drying is excessive.

3.9 Methods of Calculation

3.9.1 Calibration

Prepare standard curves by plotting the integrated peak areas as the dependent variable versus the pg standard injected as the independent variable.

Use linear regression to test for linearity and the y-intercept. Proportionality equations can be used if there is 95% or greater correlation ($R \geq 0.95$) and the y-intercept is close enough to zero so that any systematic error is less than 10%. Otherwise, concentrations of the sample solutions must be obtained directly from the standard curve provided the reproducibility of triplicate injections is within a 10% relative coefficient of variation.

3.9.2 Analyte in Sample

The residues (=R) in mg/kg of Quinclorac and its metabolite BH 514-1 can be calculated as follows:

$$R = \frac{V_E * W_A * D}{G * V_I * A}$$

G = Weight in (g)
V_E = Final volume after all dilution steps (mL)
V_I = mcL injected from V_E
W_A = Amount of determined substance read from calibration curve in ng
A = Aliquot in % (i.e., 12.5% for [(20 g/200 mL)(500 mL/2 mL) (1 mL/5 mL)])
D = Derivatization factor.

For Quinclorac:

$$D = \frac{\text{MW Quinclorac}}{\text{MW Quinclorac Methyl Ester}} = \frac{242}{246} = 0.945.$$

For BH 514-1:

$$D = \frac{\text{MW BH 514-1}}{\text{MW BH 514-1 Methyl Ester}} = \frac{707.6}{721.6} = 0.937.$$

If residues are to be reported as quinclorac equivalents multiply mg/kg BH 514-1 by the conversion factor, 1.166 (i.e., MW BAS 514/MW BH 514-1).

4 VALIDATION

4.1 BASF

Three aquatic soils collected from CA, TX and MS were spiked with BAS 514 H [3-^{14}C] (solution 375-17-2) and BH 514-1 (solution 375-76-1) to levels of 0.00, 0.010, 0.055, 0.113 ppm and subjected to the analytical method by BASF. The BAS 514 H [3-^{14}C] solution is not listed in the method as a spiking solution because its not intended to be a routine part of the method. It was only used in this study to determine extraction efficiency to differentiate any potential work up loss versus the GC/MS quantitations. All GC/MS results were converted to % recovery for evaluation

4.2 CompuChem

A second collaborative validation study was also conducted on samples prepared by BASF but analyzed by CompuChem Laboratories (Research Triangle Park, N.C.) using nonlabelled BAS 514 H and BH 514-1 at 0.01, 0.05, and 0.1 ppm (Solution 401-74-26) spiking levels. CompuChem analyzed all three levels and BASF confirmed the 0.05 ppm spiked level.

5 RESULTS AND DISCUSSION

5.1 General

Mass spectral data for BAS 514 H ME and BH 514-1 ME is shown in Figure 2. The base peaks for BH 514 H ME and BH 514-1 ME are 224 and 190 m/z and are used for selective ion monitoring (SIM) quantitation. Other ions, such as 226 and 192, may also be used for quantitation and confirmation of authentic residues.

Representative chromatograms of BAS 514 H and BH 514-1 residue analysis of the 0.05 ppm spiked CA, TX and MS soil samples are shown in Figures 3, 4, and 5, respectively. There were no interfering peaks in the controls as shown in Figures 6, 7, and 8. BAS 514 ME and BH 514-1 ME peaks are narrow and have base line resolution. The standard curve injections were all made with solutions co-injected with control sample to negate any peak enhancement by matrix effects. Peak enhancement for BAS 514 ME and BH 514-1 ME caused by matrix effects can be as great as two fold. However, as shown in Figures 9 and 10 the standard curves are linear with near zero y-intercepts.

5.2 Accuracy and Precision

5.2.1 ^{14}C-BAS 514 H Recovery Study

Recovery and precision for ^{14}C-BAS 514 H after the final TLC clean up step was excellent for all spiking levels between 0.010 and 0.113 ppm for the three soil types, TX, CA and MS. As shown in Table I, the total radioactive recovery ± std. dev. was 104% ± 9.8.

5.2.2 GC/MS (SIM) Recovery for BASF Validation Study

Recovery and precision for BAS 514 H by GC/MS was nearly identical to ^{14}C-BAS 514 H results with values ranging from 86% to 111% and a grand mean ± std. dev. of 100% ± 7.7.

Recovery and precision for BH 514-1 was also very good but more variable with a grand mean ± std. dev. of 95% ± 18.8. Results are shown in Table II.

5.2.3 GC/MS (SIM) Recovery for CompuChem Validation Study

Recovery and precision for BAS 514 H was good with a grand mean ± std. dev. 113% ± 9.0. CompuChem did not have peak enhancement due to matrix effects. Therefore, they did not co-inject control matrix with their standards. Thus, this phenomenon is probably related to the GC column rather than SIM detector.

Recoveries and precision for BH 514-1 were also excellent with a mean ± std. dev. of 97% ± 9.4. Results are shown in Table III.

5.2.4 Comparison of BASF and CompuChem GC/MS (SIM)

As shown in Table IV, there was good agreement between BASF and CompuChem for Both BAS 514 H ME and BH 514-1 ME with mean recovery values of 108% vs 119% and 108% vs 104%, respectively, for the same extract of the 0.05 ppm spiked samples. The excellent agreement between the two laboratories using different equipment and calibration procedures clearly demonstrates the ruggedness of the method.

6 CONCLUSIONS

Data presented in this report clearly show Method A8901 to be valid for the analysis of BAS 514 H and its metabolite, BH 514-1 in soils.

The use of MS (SIM) detection not only allows for a rapid work up procedure because of its selectivity but also allows for multiple ion matching or full spectra to confirm peak response as authentic BAS 514 H or BH 514-1 residues. This is extremely useful in eliminating interfering peaks which might be construed as residues by less specific detection methods.

The sensitivity of the method is good, ranging from 0.01 to 0.05 ppm depending upon soil type and instrumentation. Recoveries are quantitative for all types of soils, different spiking levels, and both compounds.

7 QUALITY ASSURANCE PROCEDURES

The raw data and analytical standards of this study are stored in the BASF archieves.

Table I. ^{14}C-BAS 514 H (LSC) Recovery Values For BASF Validation Study

	% Recovery ^{14}C-BAS 514 H				
Soil ppm	0.010	0.055	0.113	Mean	Std Dev
TX	93	103	114	103	±10.5
CA	102	102	118	107	± 9.2
MS	89	115	104	103	±13.1
Mean Std Dev	95 ± 6.7	107 ± 7.2	112 ± 7.2	104	± 9.8[a]

Book 401-81

a. n = 9

Table II. BASF GC/MS (SIM) Recovery Results For ^{14}C-BAS 514 H and BH 514-1

% Recovery for BAS 514 H

Soil \ ppm Spike	0.01	0.055	0.113	Mean	Std Dev
TX	108	105	101	105	± 3.5
CA	95	86	96	92.3	± 5.5
MS	95	111	99	102	± 8.3
Mean Std Dev	99.3 ± 7.5	101.7 ±13.1	99 ± 2.5	100	± 7.7[a]

% Recovery for BH 514-1

Soil \ ppm Spike	0.01	0.055	0.113	Mean	Std Dev
TX	87	106	92	95	± 9.8
CA	54	93	107	85	±27.5
MS	120	107	89	105	±15.6
Mean Std Dev	87 ±33	102 ± 7.8	96 ± 9.6	95	±18.8[a]

a. n = 9

1. Notebook 401-61
2. Notebook 401-64
3. Notebook 401-69

Table III. CompuChem GC/MS (SIM) Recovery Results For BAS 514 H and BH 514-1

% Recovery For BAS 514 H

Soil \ ppm Spike	0.01	0.05	0.10	Mean
TX	BDL	124	104	114
CA	BDL	116	117	117
MS	BDL	116	100	108
Mean Std Dev	BDL -	119 ± 4.6	107 ± 8.9	113 ± 9.0[b]

% Recovery For BH 514-1

Soil \ ppm Spike	0.01	0.05	0.10	Mean
TX	BDL	100	97	99
CA	BDL	112	83	100
MS	BDL	100	86	93
Mean Std Dev	BDL -	104 ± 6.9	89 ± 7.3	97 ± 9.4[b]

a. BDL = Below Detectable Limit $\leq$ 0.025 ppm

b. n = 6

Notebook reference 401-87

Table IV. Comparison of BASF and CompuChem GC/MS (SIM) Results

	% Recovery For 0.05 ppm Spike level[a]			
	BAS 514 H		BH 514-1	
	BASF	CompuChem	BASF	CompuChem
TX	106	124	94	100
CA	106	116	114	112
MS	111	116	117	100
Mean	108	119	108	104
Std Dev	± 2.9	± 4.6	±12.5	± 6.9

a. Results taken from Tables II and III.

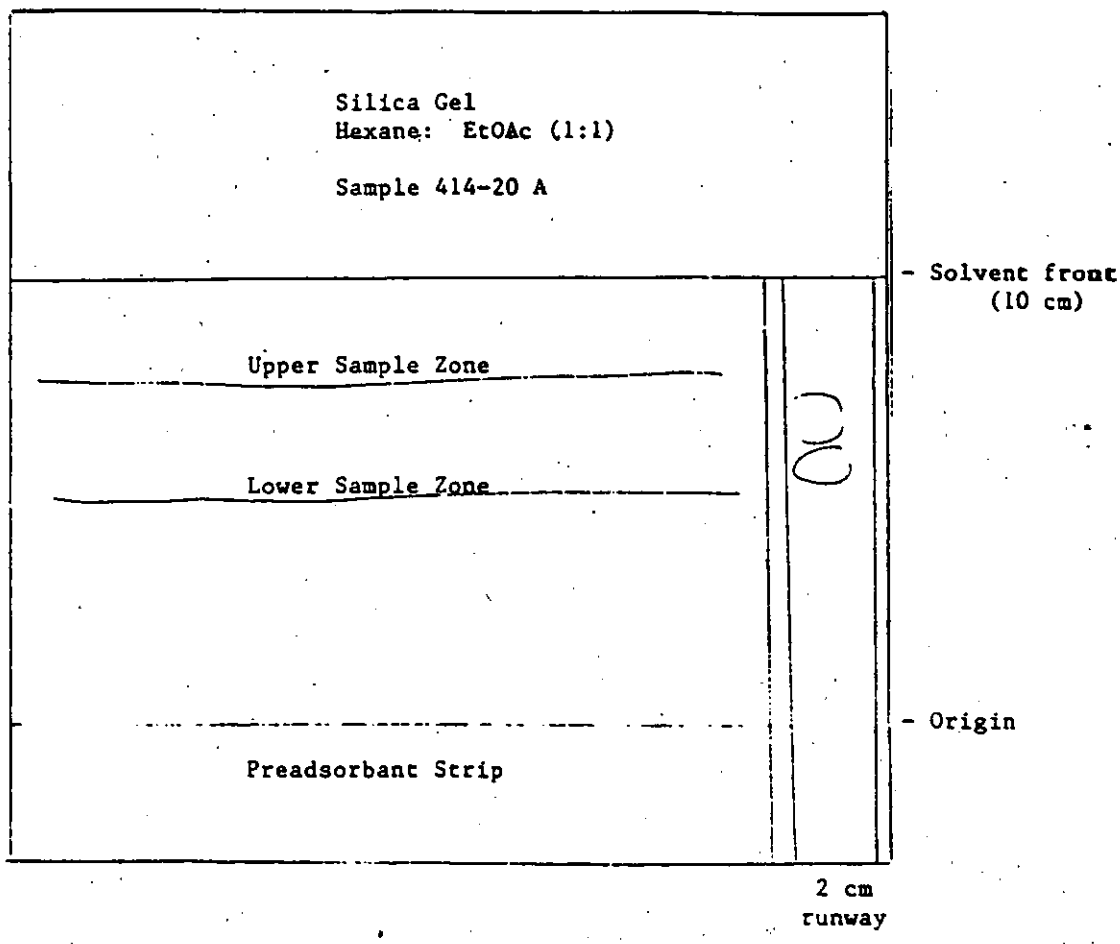


Figure 1. Representative TLC Plate After Sample Clean Up.

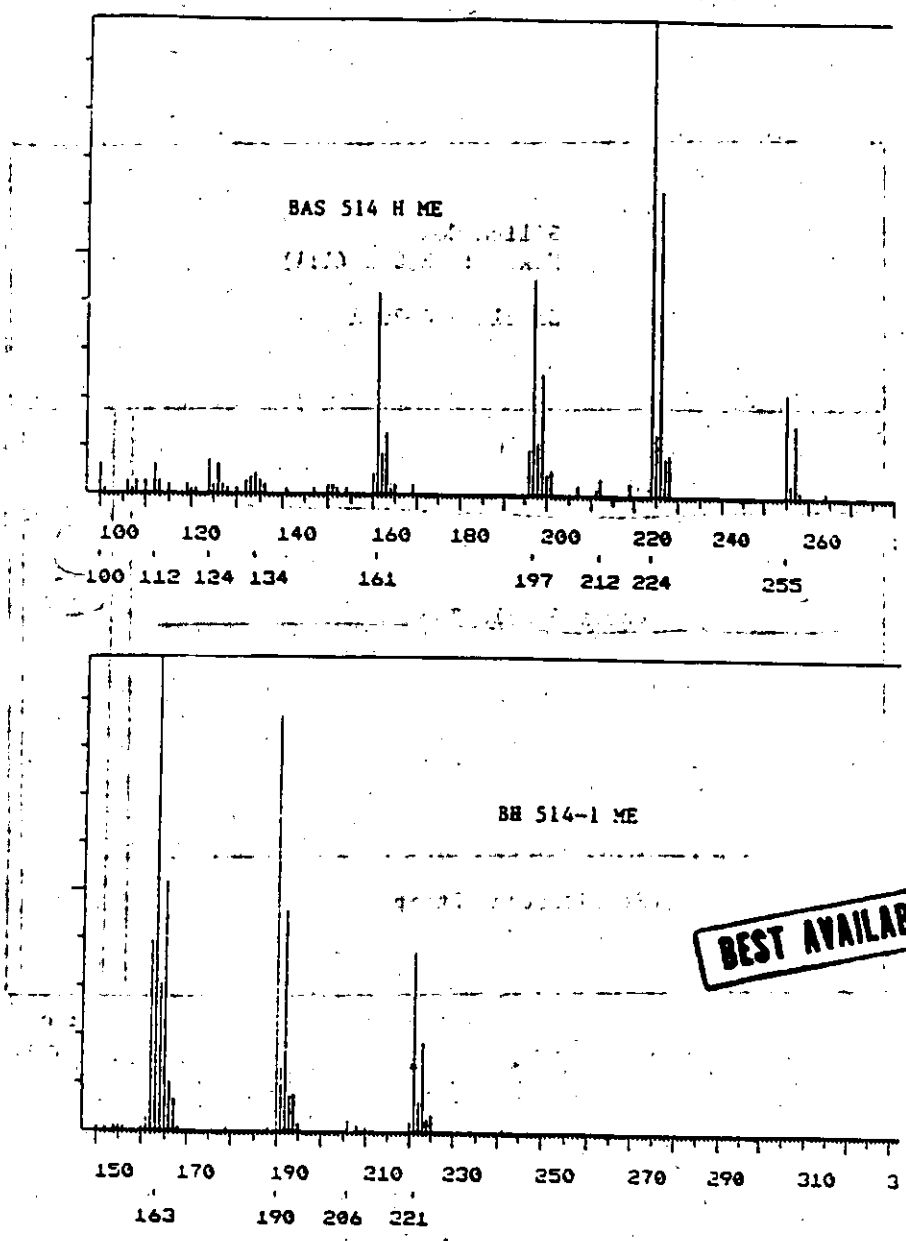
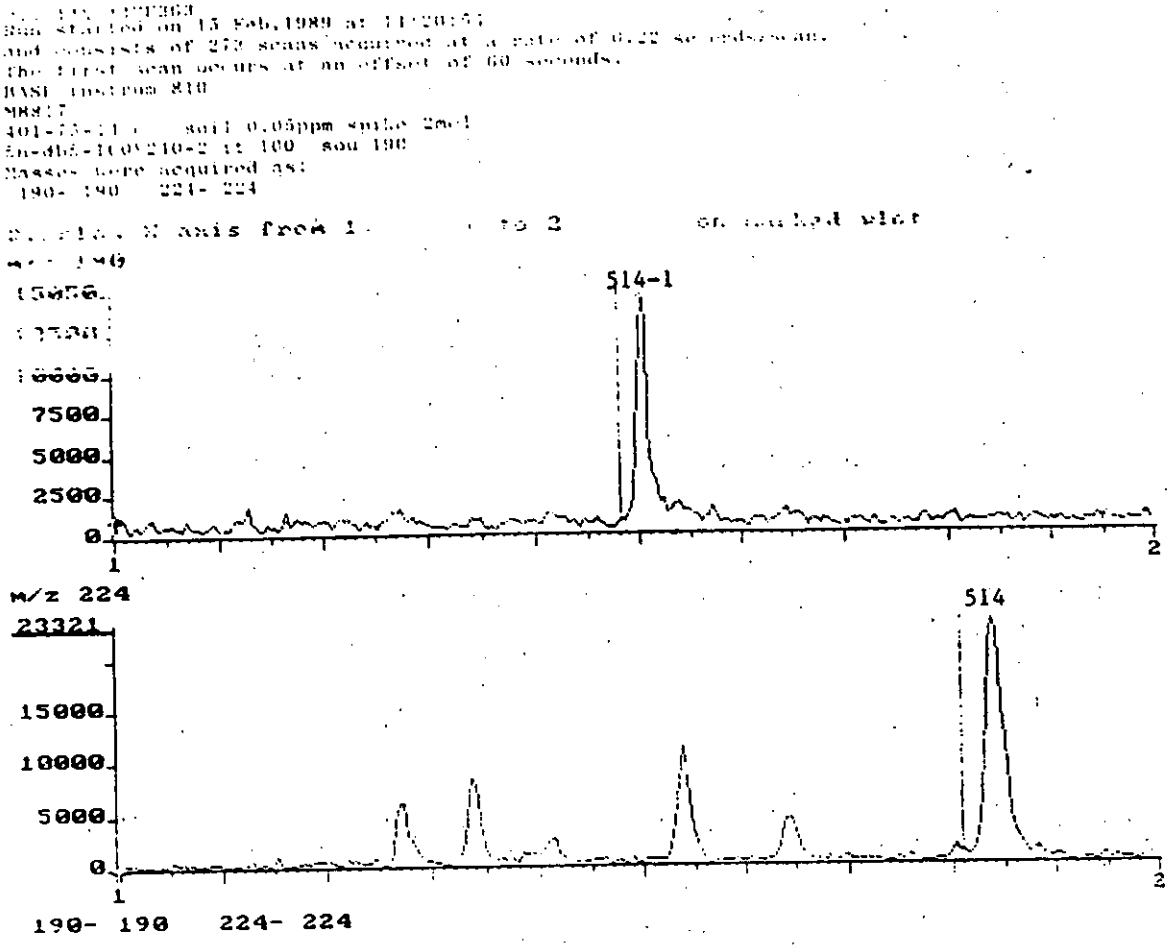


Figure 2. Mass Spectra of BAS 514 H ME and BH 514-1 ME.



190
LINE ION AREA HEIGHT BASE FROM THROUGH RT

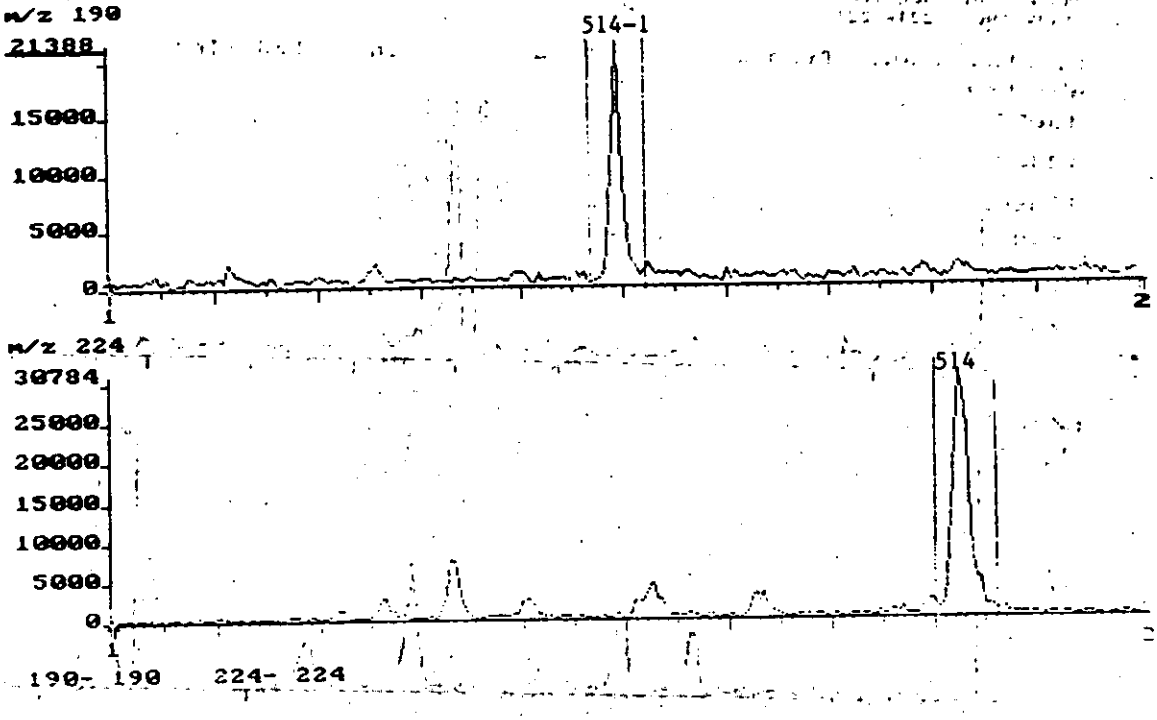
190
LINE ION AREA HEIGHT BASE FROM THROUGH RT
1 190 1.211e+004 14305 745 1.47 1.55 1.50

224
LINE ION AREA HEIGHT BASE FROM THROUGH RT
1 224 2.687e+004 22306 1015 1.82 1.87 1.84

Figure 3. Representative GC/MS (SIM) Chromatogram of BAS 514 H and BH 514-1 0.05 ppm Soiked CA Aquatic Soil.

```
D:\514\514ME366
Run started on 15 Feb,1989 at 15:01:16
and consists of 273 scans acquired at a rate of 0.22 seconds/scan.
The first scan occurs at an offset of 60 seconds.
BASF instrum 810
M8817
#01-75-10 tex soil 2mcl 0.05ppm
5n-db5-100\240-2 it 100  sou 190
Masses were acquired as:
 190- 190   224- 224
```

Display X axis from 1 to 2 on marked plot



190

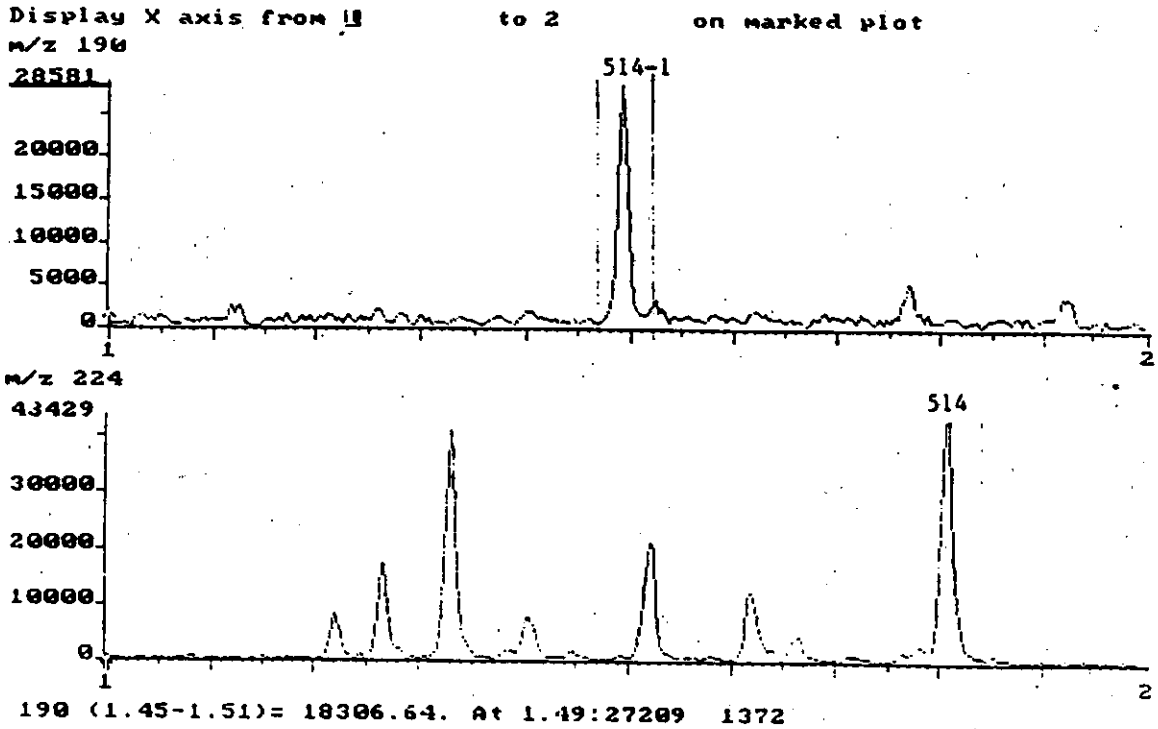
LINE	ION	AREA	HEIGHT	BASE	FROM	THROUGH	RT
1	190	1.428e+004	20602	786	1.47	1.52	1.50

224

LINE	ION	AREA	HEIGHT	BASE	FROM	THROUGH	RT
1	224	3.246e+004	29458	1326	1.81	1.87	1.83

Figure 4. Representative GC/MS (SIM) Chromatogram of BAS 514 H and BH 514-1 0.05 ppm Spiked TX Aquatic Soil.

```
D:\514\514ME368
Run started on 15 Feb,1989 at 15:24:24
and consists of 273 scans acquired at a rate of 0.22 seconds/scan.
The first scan occurs at an offset of 60 seconds.
BASF instrum 810
M8817
401-75-18 0.05ppm Spike MS 2mcl
5n-db5-100\240-2 it 100  sou 190
Masses were acquired as:
 190- 190   224- 224
```



190

LINE	ION	AREA	HEIGHT	BASE	FROM	THROUGH	RT
1	190	1.833e+004	27294	1287	1.47	1.51	1.49

224

LINE	ION	AREA	HEIGHT	BASE	FROM	THROUGH	RT
1	224	3.607e+004	0	1263	1.79	1.84	1.84

Figure 5. Representative GC/MS (SIM) Chromatogram of BAS 514 H and BH 514-1 0.05 ppm Spiked MS Aquatic Soil.

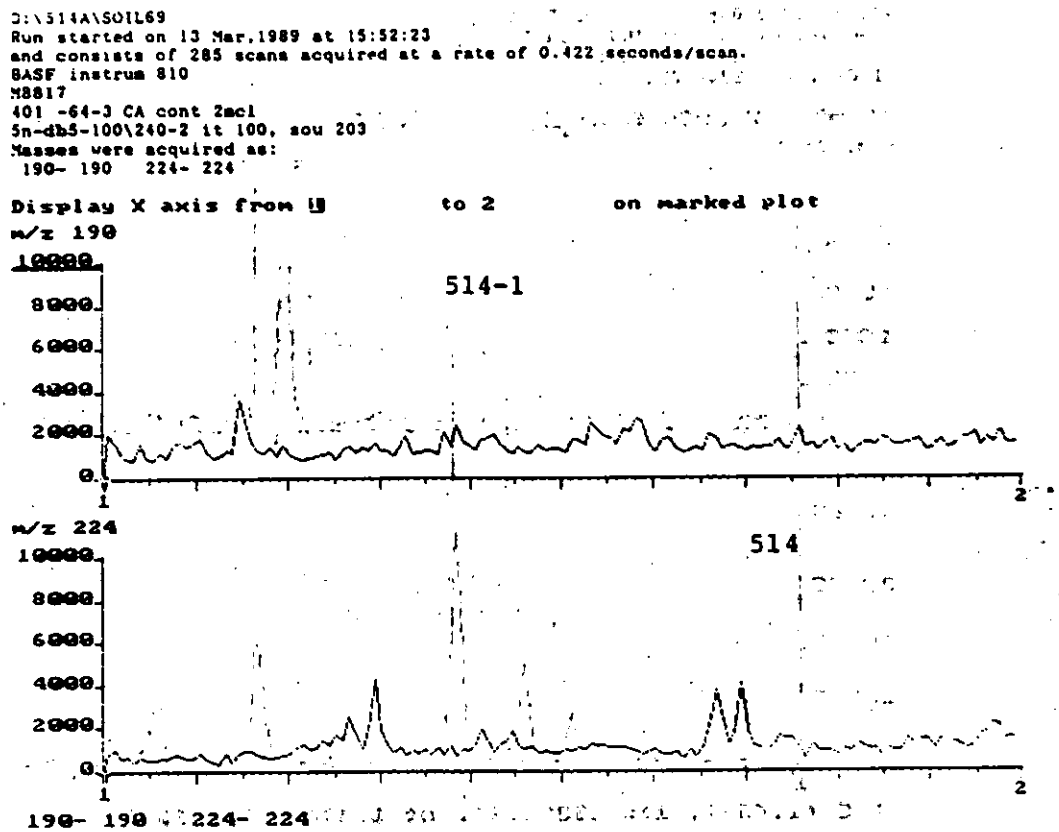


Figure 6. Representative GC/MS (SIM) Chromatogram of Control CA Aquatic Soil.

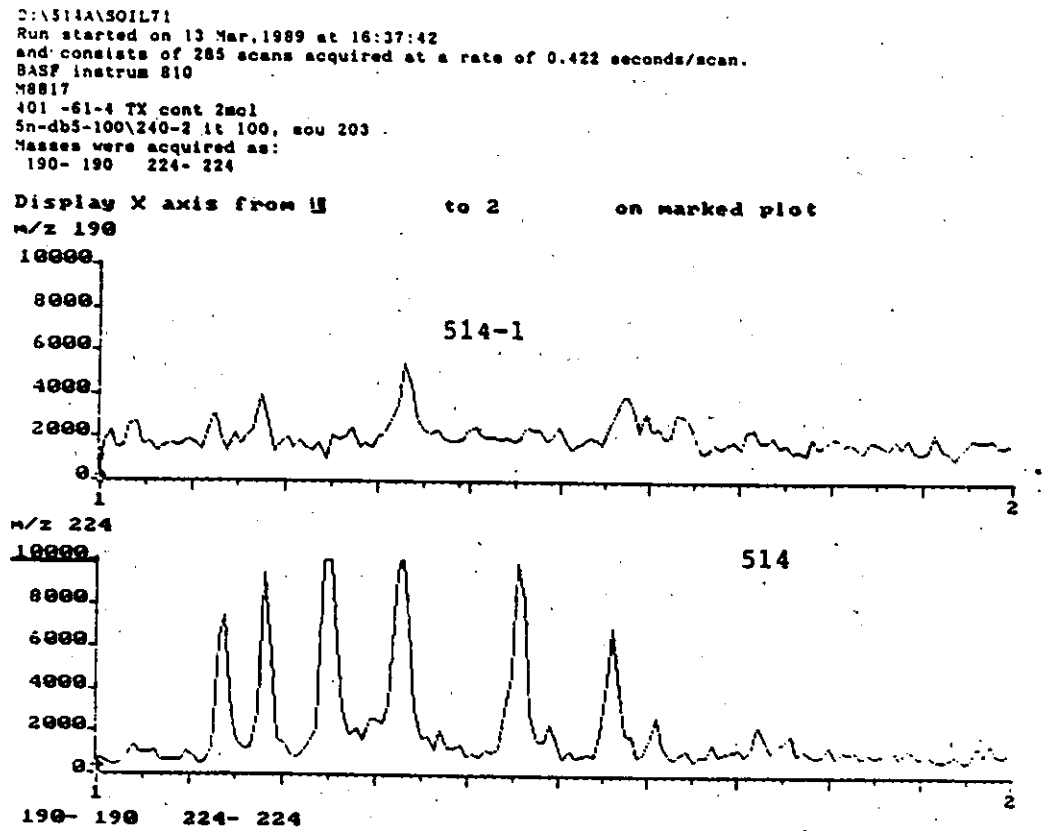


Figure 7. Representative GC/MS (SIM) Chromatogram of Control TX Aquatic Soil.

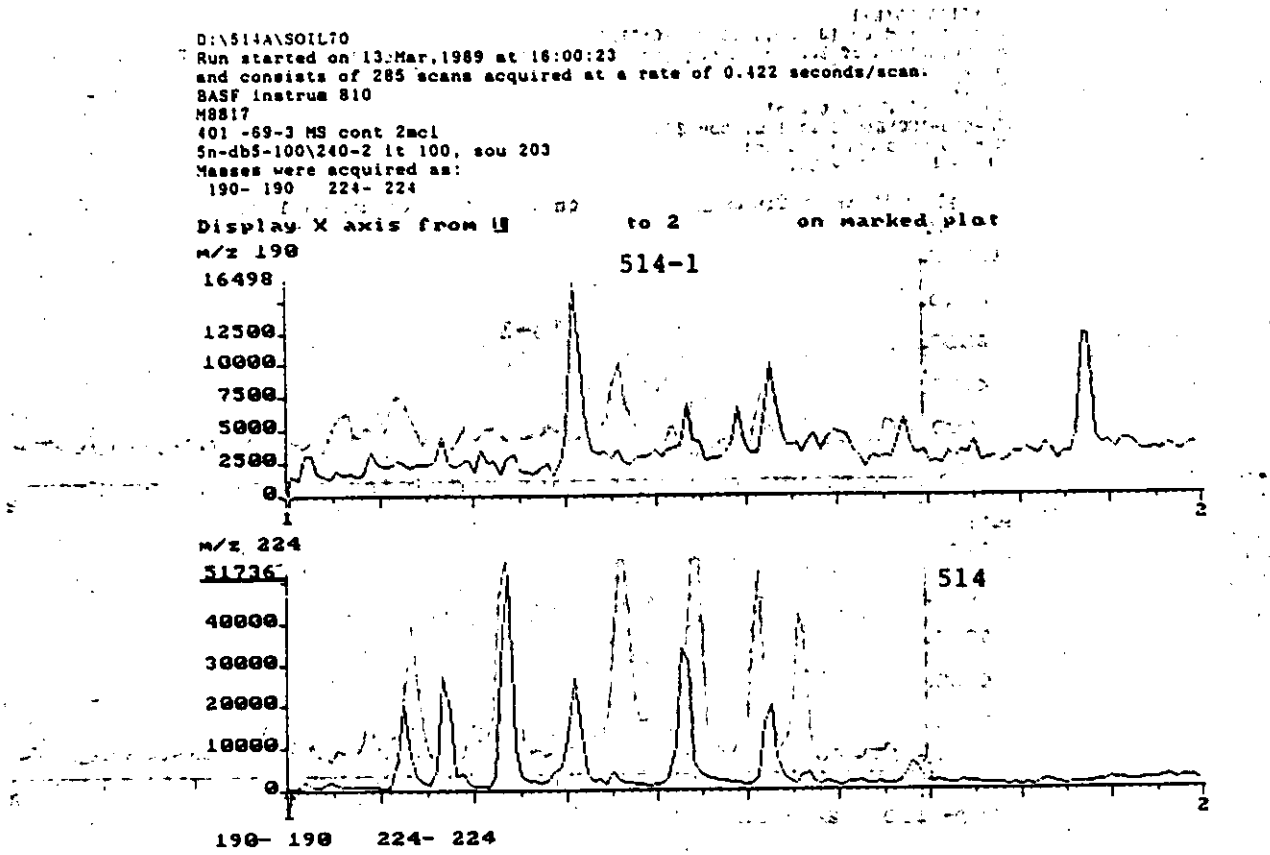


Figure 8. Representative GC/MS (SIM) Chromatogram of Control MS Aquatic Soil.

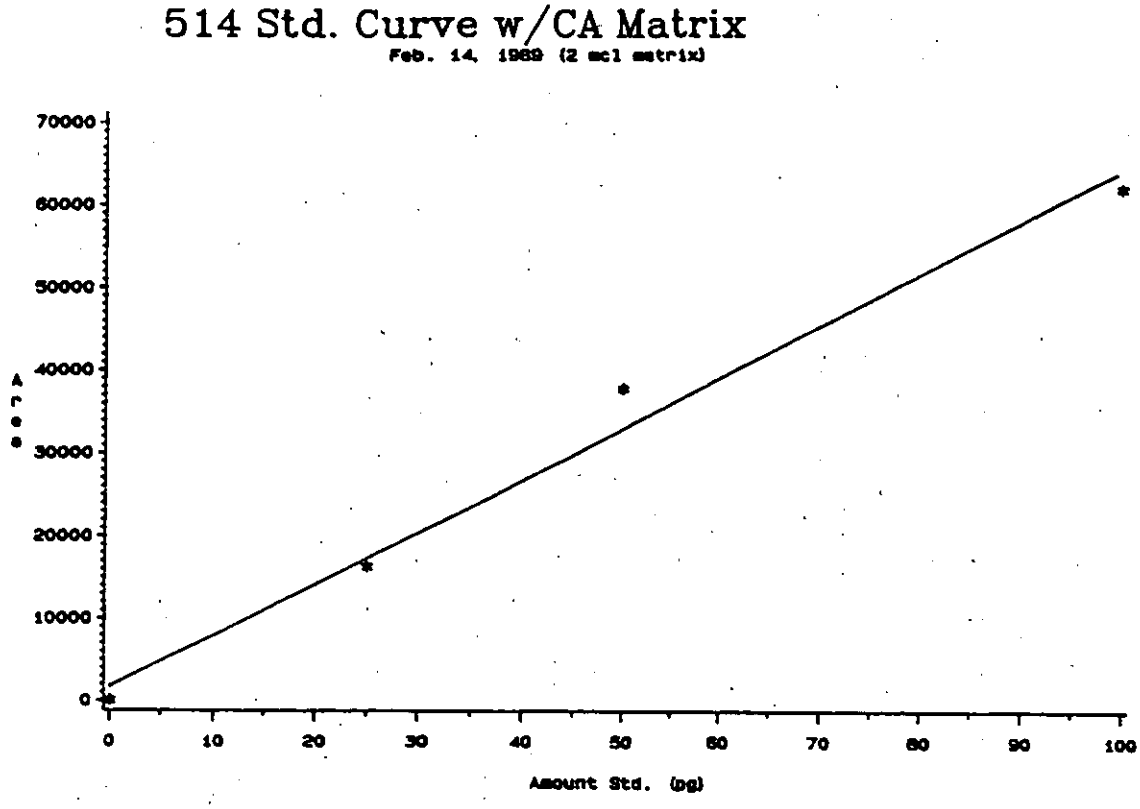


Figure 9. Representative Standard Curve for BAS 514 H ME Admixed With CA Control Soil Extracts.

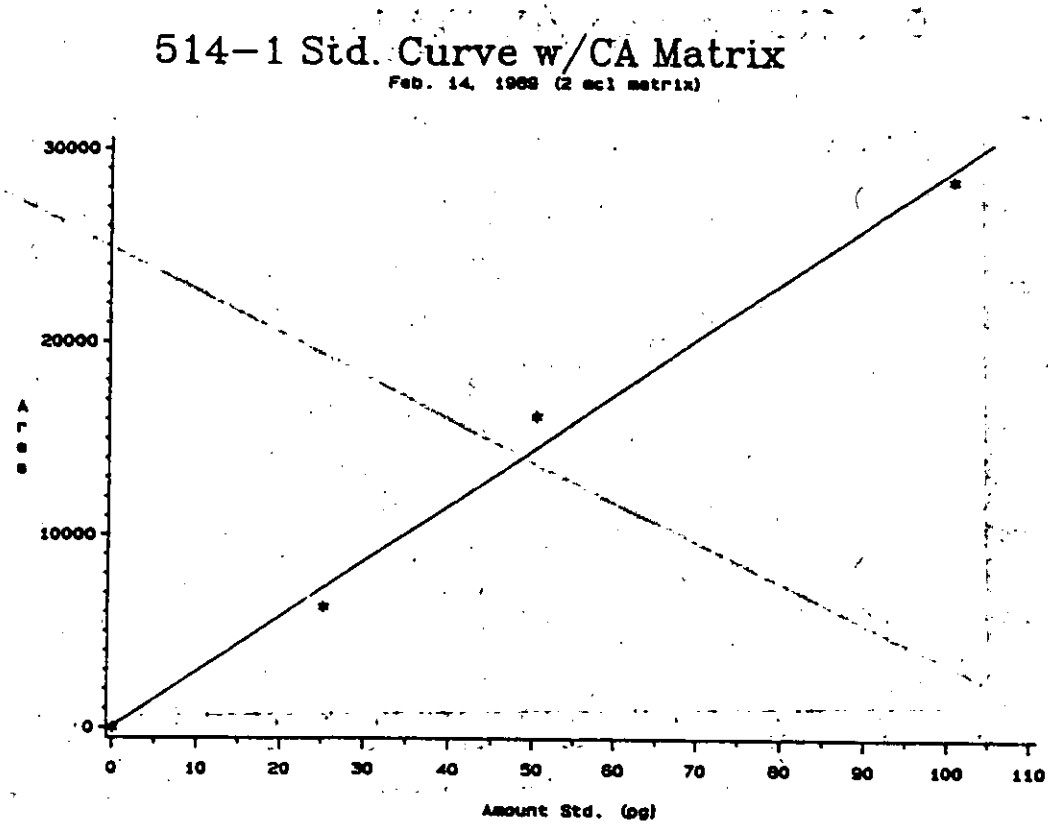


Figure 10. Representative Standard Curve for BAS 514-1 ME Admixed With CA Control Soil Extract.

END