

Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pesticide Name: Quinclorac (BAS514H)

MRID #: 440845-04

Matrix: Soil

Analysis: LC/MS/MS

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Study Title:

440845-04

RESIDUE DETERMINATIONS OF BAS 514 H (QUINCLORAC),
AND ITS METABOLITES BH 514-2-OH AND BH 514-ME IN SOIL USING LC/MS/MS

Method No. D9513
BASF Protocol 95117

Data Requirement:
Guideline 164-1

Study Completion Date:
August 7, 1996

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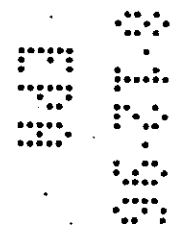
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BASF Registration Document No.

96/5149



PR 86-5 DATA CONFIDENTIALITY CLAIM

No claim of confidentiality is made for any information contained in this study on the basis of its falling within the scope of FIFRA 10 (d) (1) (A), (B) or (C).

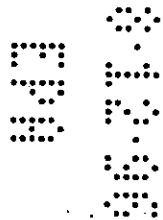
Company: BASF Corporation Agricultural Products Group

Company Agent: Robert Rohde

Date: Aug 9 1990

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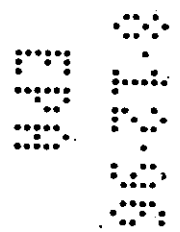
GOOD LABORATORY PRACTICES STATEMENT

This study was conducted in accordance with the requirement of 40 CFR 160, FIFRA Good Laboratory Practice standards. Amendments and deviations to the protocol are listed in Section 10.

Study Director: Jordan Date: 8-7-96

Sponsor: R. L. R. R. Date: 8/9/96

Submitter: R. L. R. R. Date: 8/9/96



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STATEMENT

of the Quality Assurance Unit

Protocol Number: 95117

Type of Study: Method Validation

The quality assurance unit of the testing facility at the ARC has inspected and/or audited these protocols and interim report and reported its findings to the study director and to management.

Date of inspection	Report to study director and to management
August 16, 1995	August 16, 1995
July 17, 1996	July 17, 1996

Marg Esy

Quality Assurance Unit

August 7, 1996

Date

STATEMENT OF THE QUALITY ASSURANCE UNIT

BASF Protocol Number: A95117
 Alta Analytical Study ID: BASNC01A-6

The Quality Assurance Unit of Alta Analytical Laboratory, Inc. has inspected and/or audited this study and reported its findings to management and the study director.

<u>Date of Inspection</u>	<u>Date Reported to Alta Management</u>	<u>Date Reported to BASF Study Director and Management</u>
10/12/95	10/31/95	11/13/95
10/30/95	10/31/95	11/13/95
3/1/96	3/19/96	4/2/96
3/3/96	3/19/96	4/2/96
4/4/96	4/5/96	4/11/96
4/8/96	4/8/96	4/18/96
5/6/96	5/6/96	5/10/96

Shelly A. Weagraff 5/31/96
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RESIDUE DETERMINATION OF BAS 514 H (QUINCLORAC),
AND ITS METABOLITES BH 514-2-OH AND BH 514-ME IN SOIL USING LC/MS/MS

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Method Number: D9513

Report Date:

ABSTRACT:

This method is for determining residues of BAS 514 H (Quinclorac) and its metabolites BH 514-2-OH and BH 514-ME in soil. For the extraction of Quinclorac and BH 514-2-OH, soil samples are first extracted with 0.1 N NaOH by shaking. For clay soils where the extraction needs to be more extensive, the samples are refluxed. The samples are centrifuged, then an aliquot is acidified and partitioned with 8:2 methylene chloride/ethyl acetate. The extract is taken to dryness by rotary evaporation, and then reconstituted into an appropriate volume of the mobile phase. If soil samples are refluxed, BH 514 ME, the methyl ester metabolite is converted to parent Quinclorac and is analyzed as parent equivalents in the method. If a shake method is used, it is necessary to analyze for the methyl ester separately. For this determination of BH 514-ME, soil samples are extracted in a mixture of methylene chloride, ethyl acetate and methanol. The extract, first separated from the soil by centrifugation, is taken to dryness by a nitrogen stream and reconstituted in an appropriate volume of mobile phase. The final quantitative determination of BAS 514 H, BH 514-2-OH, and BH 514-ME is made by LC/MS/MS using multiple reaction monitoring. The limit of quantitation for each metabolite is defined as the lowest fortification that was successfully run through the method. For this method it is 10 ppb. The average recoveries for BAS 514 was 85.3% +/- 3.6 (n=6) for the shake extraction and 95.3% +/- 7.7% (n=13) for the reflux extraction. The average recoveries for BH 514-2-OH was 81.7% +/- 4.5% (n=6) for the shake extraction and 83.6% +/- 8.4 (n=13) for the reflux extraction. The average recovery for BH 514-ME is 89.3% +/- 3.3 (n=13).

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1.0 INTRODUCTION AND SUMMARY

1.1 SCOPE AND SOURCE OF THE METHOD

1.1.1 Scope

This method is for determining residues of BAS 514 H (Quinclorac) and its metabolites BH 514-2-OH and BH 514-ME in soil. Metabolism studies show that in addition to parent Quinclorac, BH 514 2-OH and BH 514-ME are minor soil metabolites. Also, shown in metabolism studies (Reference 1), due to the acidic nature of Quinclorac a solution of sodium hydroxide is needed to free the Quinclorac from the soil. For sandy or sandy loam soils, extraction is accomplished by mechanically shaking the soil in 0.1 N NaOH for 1 hour. For soils with a clay content, it is best to use a more exhaustive extraction using a reflux of 0.1 N NaOH for 1 hour. The samples are centrifuged, then an aliquot is acidified and partitioned with 8:2 methylene chloride/ethyl acetate. The extract is taken to dryness by rotary evaporation, and then reconstituted into an appropriate volume of the mobile phase. The final quantitative determination of BAS 514 H and BH 514-2-OH is made by LC/MS/MS using multiple reaction monitoring. The methyl ester metabolite of Quinclorac, BH 514-ME, is a very minor metabolism product. When refluxing the soil in 0.1 N NaOH, this minor product is converted and analyzed as parent Quinclorac. The shake method is not sufficient to hydrolyze the ester. Therefore a separate extraction had been developed to analyze for BH 514-ME for the use in conjunction with the shake method. For this determination of BH 514-ME, soil samples are extracted in a mixture of methylene chloride, ethyl acetate, and methanol. The extract, first separated from the soil by centrifugation, is taken to dryness by a nitrogen stream and reconstituted in an appropriate volume of mobile phase. The final quantitative determination of BH 514-ME is made by LC/MS/MS.

1.1.2 Source

This method was developed at BASF Corporation, 26 Davis Drive, Research Triangle Park, North Carolina 27709 and ALTA Analytical, 5070 Robert J. Matthews Parkway, El Dorado Hills, CA 95630. This method for Quinclorac determination is a variation of BASF Method A8903 "HPLC Method for the Determination of Quinclorac (3-7-dichloro-8-quinolinecarboxylic acid) and its Metabolite BH 514-1 (3-chloro-8-quinolinecarboxylic acid) in Soil" (Reference 2) This method also extracts with sodium hydroxide and partitions with methylene chloride. Final determination of the free acid is by HPLC using column switching. The limit of quantitation of this method is 0.05 ppm. To ensure a lower limit of quantitation of at least 0.01 ppm, the method of analysis was modified to use the high sensitivity of the LC/MS/MS.

This study was initiated on August 21, 1995.

1.2 REFERENCE SUBSTANCES

Common Name:	Quinlorac		
BASF Code:	BAS 514 H		
Chemical Name:	3,7-dichloro-8-quinolinecarboxylic acid		
Empirical Formula:	$C_{10}H_5Cl_2N O_2$		
Molecular Weight:	242		
Melting Point:	Above 237°C		
Appearance:	White, Solid		
Odor:	Odorless		
Solubility - at 20°C:	(g/100 g solvent, 20°C)		
Water:	6.2 x 10 ⁻³	Toluene:	<0.1
Acetone	0.2	Ethyl acetate	0.1
Acetonitrile	<0.1	n-Hexane	<0.1
Dichloromethane	<0.1	NaOH	(0.1 N) Readily
Ethanol	0.2		Soluble
Common Name:	2-HydroxyQuinlorac		
BASF Code:	BH 514-2-OH		
Chemical Name:	3,7-dichloro-2-hydroxy-8-quinolinecarboxylic acid		
Empirical Formula:	$C_{10}H_6Cl_2N O_4$		
Molecular Weight:	258		
Common Name:	Quinlorac methyl ester		
BASF Code:	BH 514-ME		
Chemical Name:	3,7-dichloro-2-hydroxy-8-quinolinecarboxyate		
Empirical Formula:	$C_{11}H_6Cl_2N O_4$		
Molecular Weight:	256		

1.3 PRINCIPLE OF THE METHOD

For BAS 514 H (Quinlorac) and BH 514-2-OH, soil samples are extracted in 0.1 N NaOH, either on a mechanical shaker or refluxed, centrifuged and decanted. The basic extract is then acidified and partitioned with 8:2 methylene chloride/ethyl acetate. The methylene chloride extract is taken to dryness by rotary evaporation using vacuum. For BH 514-ME, soil samples are extracted in a mixture of methylene chloride, ethyl acetate, and methanol. The extract, first separated from the soil by centrifugation, is taken to dryness by a nitrogen stream and reconstituted in an appropriate volume of mobile phase. The final quantitative determination of BAS 514, BH 514-2-OH, and BH 514-ME is made by LC/MS/MS. The limit of quantitation for each metabolite is 0.01 ppm.

2.0 MATERIALS AND METHODS

2.1 Equipment	Suggested Sizes/Manufacturer
Rotary evaporator:	Buchi Rotovapor or equivalent
N-Evap (Nitrogen Stream)	Organomation Assoc. or equivalent
Centrifuge:	IPC PR 700 Refrigerated or Equivalent
Mechanical shaker:	Janke & Kunzel HS 501D
Mini Centrifuge:	Capsule HF-120 Millipore or equivalent 1.5m/0.45 micron nylon
Centrifuge filter for mini-centrifuge:	MSI or equivalent
Separatory funnels:	250 mL, 125 mL
Flat bottom flasks:	300 mL
Centrifuge glass tubes with teflon lined screw top flasks	50 Fisher Scientific
Glass Bottles	50 mL
Volumetric flasks:	10, 25, 50, 100 mL
Volumetric pipettes:	0.5, 1, 5, 10, 25 mL
Graduate pipettes:	1 mL
Long stem funnels:	75 mm id
Conical inserts:	200 μ L Varian or equivalent
Autosampler vials:	1.5 mL Varian or equivalent
Phase Separator Paper:	15.0 cm 1 PS
Magnetic stirring bars	2.5 cm
Reflux condenser	Standard joint
Stirring hot plate	Corning PC-351
Ultrasonic Bath	Branson 1200
Top loading balance	
Other general laboratory glassware and supplies.	

Preparations for Mobile phases:

Mobile phase A: Add 100 mL 50mM ammonium acetate and 1 mL of formic acid to 900 mL of water

Mobile Phase B: Add 100 mL 50mM ammonium acetate and 1 mL of formic acid to 900 mL of methanol

2.2. Reagents and Chemicals

Methylene Chloride

Acetonitrile

Methanol

Water

Ethyl Acetate,

Formic Acid 95-97%

Hydrochloric Acid

Ammonium Formate

Ammonium Acetate

Sodium Hydroxide

Suggested Source/PreparationBaxter Healthcare Corporation, B&J Brand
CAS 75-09-2Baxter Healthcare Corporation, B&J Brand
CAS 67-56-1Baxter Healthcare Corporation, B&J Brand
CAS 67-56-1Baxter Healthcare Corporation, B&J Brand
CAS 7732-18-5Baxter Healthcare Corporation, B&J Brand
CAS 111-90-0Aldrich Chemical cat#10,652-6
CAS 64-18-6Aldrich Chemical cat#25,814-8,
CAS 7647-01-0Aldrich Chemical cat#15,626-4
CAS 540-69-2Aldrich Chemical cat#37,233-1
CAS 631-61-8Aldrich Chemical cat#31,951-1
CAS 1310-73-22.3 Standard Substances and Solutions

Standards Used:

BASF Code	Lot Number	Purity
BAS 514 H	39/182-1	99.0%
BH 514-ME	L33/215	99.9
BH 514-2-OH	00820-63	98.6%

Standards supplied by:

BASF Corporation
Agricultural Products Group
P. O. Box 13528
Research Triangle Park, NC 27709

Standards are to be maintained frozen ($<-5^{\circ}\text{C}$) until its use. Standards were characterized as required by 40 CFR part 160, FIFRA Good Laboratory Practices. Information on the synthesis and subsequent characterization of these substances is available to BASF and is located at BASF Corporation, Agricultural Products Group, Research Triangle Park, North Carolina.

Solutions of standards are to be refrigerated ($+4^{\circ}\text{C}$) during their use in this study. Stock solutions (1 mg/mL) are to be made fresh every three months. Dilutions of the stock solution are to be made monthly.

2.3.1 Standard Solutions for Fortifications

NOTE: Storage containers for standard solutions are amber bottles with Teflon®-lined screw caps. These concentrations are suggested. Different preparation and concentration schemes may be used and additional standard concentrations may be prepared and used as needed.

Stock Solution Preparation

Prepare a 1.0 mg/mL BAS 514, BH 514-ME, and BH 514-2-OH (powder) stock solution by separately weighing an appropriate amount into separate volumetric flasks. Use methanol as the solvent. For example, weigh 25.0 mg of Quinclorac into a 25.0 mL volumetric flask. Dissolve with methanol and dilute to the mark.

NOTE:

The solubility of BH 514-2-OH is best achieved by adding 100 µg of 1 N NaOH. After addition of base dilute to the mark with methanol.

Prepare a 100.0 µg/mL combined standard solution by transferring an appropriate amount of each of the 1.0 mg/mL stock solution with a volumetric pipet into a volumetric flask (typically 5 mL of 1.00 mg/mL stock solution into a 50 mL volumetric flask). Dilute to the mark with methanol.

Prepare the 10.0 and 1.0 µg/mL standard solutions by making dilution of the 100.0 µg/mL solution with methanol.

Prepare 0.1 µg/mL standard solutions by making dilution of the 1.0 µg/mL solution.

2.3.2 Standard Solutions for LC/MS/MS Analysis

Prepare the 50, 20, 10 and 5 pg/µl standard solutions by making dilution of the 2.0 µg/mL solution with 50:50 methanol/50 mM Ammonium Acetate solution. For example, to prepare 50 pg/µl solution pipet 2.5 ml of 2.0 µg/ml solution into a 100.0 mL volumetric flask. Dilute to the mark with 50:50 methanol:water.

3.0 ANALYTICAL PROCEDURES-

3.1. QUINCLORAC AND BH 514-2-OH EXTRACTION

Samples are homogenized first by grinding with an appropriate mill with dry ice to maintain the integrity of the samples

- 3.1.1 Weigh 10.0 g of a soil sample using a top loading balance into a 150 mL glass centrifuge bottle. FOR SOILS WITH A HIGHER CLAY CONTENT A REFLUX EXTRACTION IS NEEDED: Weigh 10.0 g of soil into a 250 mL Erlenmeyer flask equipped with ground glass neck. Add a teflon encased stirrer appropriate for the size flask. As required, fortify control samples with appropriate volumes of fortification solutions. Go to Step 3.2.1

NOTE Fortifications for Procedural Recoveries

It is recommended that at least two fortifications and one untreated sample (control) are run with each set of samples to monitor method efficiency. Typically, one fortification sample at the limit of quantitation is run along with one fortification sample at a higher level. For each fortified sample, an appropriate volume of standard solution is added to a control soil sample by volumetric pipet. For example, for a 0.01 ppm fortification, pipet 1.0 mL of the 0.1 µg/mL standard solution into the control sample. Fortifications are made into the sample before the 0.1 N NaOH is added to the sample for the initial extraction.

3.2 EXTRACTION OF RESIDUE

FOR SHAKE EXTRACTION

- 3.2.1 Add 50.0 mL of 0.1 N NaOH and shake for 1 hour using the mechanical shaker. Centrifuge the sample for 15 minutes at 3500 rpm, or until the soil is completely separated from the extract and the supernatant is clear, then carefully pipette a 25 ml aliquot into a 250 ml separatory funnel. The centrifugation step is very important! If the supernatant is not clear and free of particulates, repeat. Go to Step 3.2.2
- 3.2.2 Add approximately 1 mL HCl to the 25 mL aliquot to change the pH to <2.0. Go to Step 3.3.1.

For Reflux Extraction

- 3.2.1.1 Add 50.0 mL of 0.1 N NaOH to the Erlenmeyer flask and reflux for 1 hour using chilled-water condensers and a hot plate equipped with a stirrer. Stir the soil softly and check the apparatus frequently to prevent the sample foaming and boiling over. After 1 hour, let the sample cool, then carefully pour most of the mixture into a centrifuge tube. It is not necessary to get all of the solution and do not rinse the bottle. Centrifuge the extract for 15 minutes at 3500 rpm, or until the soil is completely separated from the extract and the supernatant is clear, then carefully pipette a 5 ml aliquot into a 125 ml separatory funnel. Save a portion of the solution left in the bottle for re-analysis if necessary. The centrifugation step is very important! If the supernatant is not clear and free of particulates, repeat. Go to Step 3.2.2.1.
- 3.2.2.1 Add approximately 0.5 mL 88% formic acid to the 5 ml aliquot to change the pH to <2.0. For both, measure the pH with pH indicator strips. Go to Step 3.3.1.1.

3.3 METHYLENE CHLORIDE PARTITION CLEAN-UP

For Shake Extraction

- 3.3.1 Extract the aqueous contents (25 mL) of the separatory funnel with a 50 mL portion of dichloromethane: ethyl acetate (8:2). Shake the funnel for 2 min, and allow the layers to separate. Separate the organic layer and pass through phase separation paper into a 250 mL round flat bottom. Do not take emulsions! Repeat twice more for a total of 3 partitions. Rinse the phase separation paper with the methylene chloride:ethyl acetate solvent, and add the rinse to the flask. Go to Step 3.3.2.

NOTE: The centrifuge step 3.2.4 should have removed all particulates that will cause emulsions. Let the samples sit until total separation. If necessary the sample can be centrifuged to aid separation.

- 3.3.2 Concentrate the combined extracts to 5-20 mL using a rotatory evaporator with water bath at 40 \pm 5 $^{\circ}$ C. Transfer the extract to a test tube using methylene chloride as a rinse and nitrogen evaporate to dryness in a water bath at 40 \pm 5 $^{\circ}$ C.

For Reflux Extraction

- 3.3.1.1 Extract the aqueous (5 mL) of the separatory funnel twice with 20 mL (2 x 20 = 40 total volume) portions of dichloromethane: ethyl acetate (8:2). Shake the funnel for 2 min, and allow the layers to separate. Separate the organic layer and pass through phase separation paper into a 50 mL glass container. Cap the 50 mL glass container and shake. Remove a 20 mL aliquot and transfer to a 50 mL round bottom flask. Go to 3.3.1.2.

- 3.3.1.2 Concentrate the combined fraction to 5 mL using a rotatory evaporator with water bath at 40 \pm 5 $^{\circ}$ C. Transfer the extract to a test tube using methylene chloride as a rinse, and nitrogen evaporate to dryness in a water bath at 40 \pm 5 $^{\circ}$ C.

3.4 LC/MS/MS ANALYSIS SAMPLE PREPARATION

- 3.4.1 For the control, 0.01 ppm procedural and samples, add 0.5 mL methanol/ 50 mM ammonium acetate (1:1) to the dry extract residue, vortex and sonicate for approximate 2 minutes. Dilute other procedural fortifications as needed. Filter through a 0.45 micron nylon filter capsule or centrifuge on the mini centrifuge until all the solution has been filtered.
- 3.4.2 Place a 200 μ L conical insert into a 1.5 mL glass auto sampler vial. Transfer the filtered solution into the 200 μ L conical insert in the 1.5 mL glass autosampler vial.

3.5 BH 514-METHYL ESTER - EXTRACTION OF RESIDUE

- 3.5.1 Weigh 10.0 g of a soil sample using a top loading balance into a 150 mL glass centrifuge bottle. As required, fortify control samples with appropriate volumes of fortification solutions.
- 3.5.2 Add approximately 10 g of sodium sulfate to each tube. Add 40 mL of (1:1:1) methanol/methylene chloride/ethyl acetate and shake for 1 hour using the mechanical shaker. Centrifuge the extract for 15 minutes at 3500 rpm, or until the soil is completely separated from the extract and the supernatant is easy to pour, then carefully pipette a 4 mL aliquot into a 16 mL test tube.

3.5.3 Concentrate the fraction to dryness using a nitrogen stream with water bath at 40°-45°C. For the control, 0.01 ppm fortification, and samples, dissolve the residue in 2.0 mL of methanol, vortex and sonicate. Add 2.0 mL of 50 mM ammonium acetate and vortex. Dilute other procedural fortifications as needed.

3.5.4 Filter sample through a 0.45 micron nylon filter capsule directly into a autoinjector vial.

3.6 INSTRUMENTATION

3.6.1 Description of Instrument

Instrument: PE SCIEX API III plus LC/MS/MS SYSTEM triple quadrupole mass spectrometer equipped with Electro Spray Ionization

HPLC: Shimadzu LC-10AD HPLC pumps (2) with SCL-10A controller and SIL-10A Autoinjector (or equivalent)

Injector: Thermo Separation Products Spectra System Autosampler 3000

Column: 50 x 2 mm Metachem Inertsil 5 ODS2

Data System: Apple Macintosh Quadra 900 Data System (PE Sciex Software)

Other equivalent hardware may be used.

**INSTRUMENT CONDITIONS ARE SPECIFIC PER EXTRACTION!
PLEASE CHECK CAREFULLY WHICH TO USE!**

3.6.2.1: Analysis of Quinclorac and 2-OH-Quinclorac Shake Extraction Samples

HPLC Operating Conditions:

Column: 50 x 2 mm Inertsil 5 ODS2, P/N 0296-050-020 (Metachem Technologies, Torrance, CA (310) 793-2300)

Mobile Phase A: Water with 0.1% formic acid and 5 mM NH₄AOc

Mobile Phase B: Acetonitrile with 0.1% formic acid

Flow Rate: 0.4 mL/min with -1:10 post-column split (Valco tee or equivalent)

Gradient (A/B): 90/10 (Hold 1 minute) to 10/90 at 7 minutes
Re-equilibrate for 7.1 minutes

Injection Vol.: 25 µL

Note: The total void volume for the system used to develop this method was ~0.6 mL. Gradient times may need to be modified to provide similar chromatography using different LC systems.

API Instrument Parameters:

Note: The following recommended instrument parameters were found to be optimal for the instrument used for the method validation. See Spectra in Figure 3. The exact values used must be optimized for each instrument.

Mode:	Negative Ion Ionspray
ISV Voltage:	-3 kV
Orifice:	-56 V
Curtain Gas:	Nitrogen @ 1L/min
Nebulizer Gas:	Nitrogen @ 80 psi

Auxiliary Gas: Nitrogen @ 1L/min
 Interface Setpoint: 55°C
 Collision Gas: Argon at -290 eV
 Collision Offset (R0/R2): -30V/-23V
 Resolution: Increase DM1 and DM3 by 0.2 units from normal PPG values for extra sensitivity if needed.

Acquisition Parameters:

Delay: 4 minutes
 Dwell: 750 msec
 Acquire: 3 min
 Settling Mass: 100.

Analyte	Precursor/Product Ions (m/z)	Retention Time (approx)
BAS 514 H	240/196 ± 0.2	5:10
BAS 514-2-OH	256/212 ± 0.2	4:40

Analysis Of Quinlorac and 2-OH-Quinlorac Reflux Extraction Samples**HPLC Operating Conditions:**

Column: Betasil C18, 100 x 2 mm, P/N 105-701-2-CPF, Keystone Scientific, State College, PA (814) 353-2300
 Guard Column: Betasil, 20 x 2 mm Javelin, P/N 88202-701-P
 Mobile Phase A: Water with 0.1% formic acid and 5 mM NH4OAc
 Mobile Phase B: 9:1 Methanol/ 5mM NH4OAc with 0.1% formic acid
 Flow Rate: 0.3 mL/min with ~1:3 post-column split (Valco tee or equivalent)
 Injection Vol.: 20 µL
 Gradient (A/B): 90/10 to 10/90 at 9 minutes
 Re-equilibrate at 13 minutes

Note: The total void volume for the system used to develop this method was ~0.6 mL. Gradient times may need to be modified to provide similar chromatography using different LC systems.

API Instrument Parameters:

Note: The following recommended instrument parameters were found to be optimal for the instrument used for the method validation. The exact values used must be optimized for each instrument used for analysis and documented in the raw data.

Mode: Positive Ion TurbolonSpray
 ISV Voltage: 4.5 kV
 Orifice: 50 V
 Curtain Gas: Nitrogen @ 1.2 L/min
 Nebulizer Gas: Nitrogen @ 80 psi
 Auxiliary Gas: Nitrogen @ 6 L/min
 Turbo Temperature: 470 °C
 Interface Setpoint: 65 °C
 Collision Gas: Argon at -290 eV
 Collision Offset (R0/R2): 30V/0V

Resolution: Increase DM1 and DM3 by 0.2 units from normal PPG values for extra sensitivity if needed.

Acquisition Parameters:

Delay: 7 minutes
 Dwell: 750 msec
 Acquire: 2.5 min
 Pause: 0.02msec
 Settling Mass: 100

Analyte	Precursor/Product Ions (m/z)	Retention Time (approx)
BAS 514 H	242/161	8:30
BAS 514-2-OH	258/184	7:55

Analysis of Quinclorac Methyl EsterHPLC Operating Conditions:

Column: Betasil C18, 100 x 2 mm, P/N 105-701-2-CPF, Keystone Scientific, State College, PA (814) 353-2300
 Guard Column: Betasil, 20 x 2 mm Javelin, P/N 88202-701-P
 Mobile Phase A: water with 5mM NH₄OAc and 0.1% formic acid
 Mobile Phase B: 9:1 Methanol/ 5mM NH₄OAc and 0.1% formic acid
 Flow Rate: 0.4 mL/min with ~1:10 post-column split (Valco tee or equivalent)
 Injection Vol.: 20 µL
 Gradient (A/B) Isocratic @ 40/60

Note: The total void volume for the system used to develop this method was ~0.6 mL. Gradient times may need to be modified to provide similar chromatography using different LC systems.

API Instrument Parameters:

Note: The following recommended instrument parameters were found to be optimal for the instrument used for the method validation. The exact values used must be optimized for each instrument used for analysis and documented in the raw data.

Mode: Positive Ion Turbo Ionspray
 ISV Voltage: 4 kV
 Orifice: 65 V
 Curtain Gas: Nitrogen @ 1.2 L/min
 Nebulizer Gas: Nitrogen @ 80 psi
 Auxiliary Gas: Nitrogen @ 6 L/min
 Turbo Temperature: 470 °C
 Interface Setpoint: 65 °C
 Collision Gas: Argon at ~290 cgt
 Collision Offset (R0/R2): 30V/15V
 Resolution: Increase DM1 and DM3 by 0.2 units from normal PPG values for extra sensitivity if needed.

Acquisition Parameters:

Delay: 3.5
Dwell: 750 msec
Acquire: 2.5 min
Pause: 0.02 msec
Settling Mass: 100

Analyte	Precursor/Product Ions (m/z)	Retention Time (approx)
BAS 514-Me	256/224 ± 0.2	4:10

3.6.3. Calibration Procedures

The standard curve is derived using the area response of the analytes (y) versus the concentration of the native compounds (x) from all standards injected with the analysis set. A weighted linear regression (1/x) standard curve is used for quantitation of all samples.

A five point calibration curve must be used for quantitation of sample extracts. At least two standards at each concentration must be injected in an analysis set.

Instrument analysis must begin and end with the injection of a standard. No more than three samples may be injected between standard injections.

Acceptance of each sample set will be made by evaluation of the correlation coefficient of the standard curve for each analyte. Correlation coefficients must be >0.98.

3.6.4. Sample Analysis

Three separate analytical conditions are described. The first method for the analysis of Quinclorac and 2-OH-Quinclorac by the shake extraction, uses a 50 x 2 mm column and negative ionization. The second method used for the analysis of Quinclorac and 2-OH-Quinclorac by the Reflux Extraction which produces extracts with a high matrix content uses a longer analytical column (100' x 2 mm), different organic modifier, and turbo ionspray to enhance sensitivity. A third method is described for analysis of the methyl ester by positive ionization using turbo ionspray.

Standards and extracts are analyzed using a reversed phase liquid chromatography analytical column interfaced to a triple stage mass spectrometer using ionspray atmospheric pressure ionization (API). Turbo-ionspray is used to enhance sensitivity in two of the three analysis methods described.

A post column split (~1:10) is used for the analyses. A Valco Tee is connected to the bulkhead fitting on ionspray flange using a short piece of 0.007" tubing. Connect a piece (~370 mm) of 100 micron fused silica capillary tubing to the other side of the bulkhead fitting, and thread the free end of the fused silica tubing through the ionspray needle to within about 1 mm from the end. Connect the column to the tee using a short piece of 0.007" tubing. Connect an appropriate length of tubing to the tee to provide the desired split. This piece is placed in a waste container during analysis. A good start is to use a 5

foot piece of 0.007" peek tubing for the length of fused silica specified above. Lengthen or shorten the fused silica or waste tube as appropriate to obtain the desired split.

Inject 20 or 25 µl of sample into the LC/MS/MS as described above. Directly compare peak area of unknown samples injected with the standard curve to obtain pg of BAS 514, BH 514-2-OH or BH 514-ME in the sample.

Bracket every 1-3 samples with standards to check for shifts in sensitivity. If the peak area of the unknown is larger than the highest standard, dilute the unknown appropriately and reinject. It is good practice occasionally to inject solvent (methanol) blanks to ensure that BAS 514, BH 514-2-OH, or BH 514-ME are not carried over from run to run.

3.7 INTERFERENCES

3.7.1 Sample Matrices

Ionization suppression has been observed from with extracts generated by the reflux method. The use of methanol as an organic modifier, combined with a longer column and turbo ionspray reduces the suppression effect. Verification that suppression has been controlled can be determined by analysis of matrix fortification samples. If interfering peaks occur in the chromatogram that can not resolved, analyze another aliquot of the extract from 3.2.1.1 by BASF Method A8903 for quinclorac. (Reference 2)

3.7.2 Other Sources

Other Pesticides:	None known to date
Solvents:	None known to date
Labware:	None known to date

3.8 CONFIRMATORY TECHNIQUES

Due to the high specificity of the MS/MS, analyzing product ions, a confirmatory technique is not necessary.

3.9 TIME REQUIRED FOR ANALYSIS

1. Shake Extraction

Extraction and Analysis of extracts generated by the shake method takes approximately 5 hours and 5 hours, respectively for 17 samples

2. Reflux Extraction

Extraction and Analysis of extracts generated by reflux extraction takes approximately 6 hours and 8 hours respectively for 17 samples

3. Methyl Ester Method

Extraction and Analysis of extracts generated for the methyl ester takes approximately 3 hours and 5 hours, respectively for 17 samples.

3.10 POTENTIAL PROBLEMS

Sodium hydroxide extractions of soils are exhaustive and may remove different components of soils which vary from region to region. In Step 3.3, emulsions may form more easily in soils with higher organic contents. If emulsions do form, centrifugation of the extract will aid in partitioning.

4.0 METHODS OF CALCULATION**4.1 CALIBRATION**

Construct a linear least squares working curve in the form $y = bx + c$ from the standards by plotting peak area versus weight of standard injected.

4.2 ANALYTE IN SAMPLE

Calculate results based on peak area measurements. Using the peak area measurements for BAS 514 H, BH 514-2-OH, BH 514-ME in the samples, determine the amount of BAS 514 H, BH 514-2-OH, BH 514-ME from the least squares working curve.

Calculate ppm values by the equation below.

$$\text{ppm} = \frac{A}{B \times 1000}$$

where A = pg value interpolated from standard curve

$$B = \text{mg Sample Injected} = \frac{\text{sample wt. (g)} \times \text{ul injected}}{\text{Final dilution volume (mL)}}$$

The "final dilution volume" includes any dilutions which have been made.

4.3 CALCULATION OF PROCEDURAL RECOVERIES

Correct fortification results for residues found in the control sample as follows:

$$\text{ppm (corrected)} = \text{ppm in fortified control} - \text{ppm in control}$$

Determine percent recovery from the fortification experiments as follows:

$$\% \text{ Recovery} = \frac{\text{ppm X 100}}{\text{ppm BAS 514 and BH 514-2-OH added}}$$

Do not correct treated sample results for either control residues or procedural recoveries.

5.0 VALIDATION

Validation of this method was done by ALTA Analytical Laboratories.

Control soil samples from a sandy loam site were homogenized at BASF and sent frozen by overnight carrier to ALTA Laboratories. These control samples were given a unique laboratory control number by ALTA. Control samples were fortified with an appropriate amount of BAS 514, BH-514-2-OH or BH 514-ME at 0.01 ppm, 0.10 ppm, 0.40 ppm or 1.0 ppm. There were duplicate samples for each fortification level. A blank control was run with the set. The validation results are in Table 1, 3 and 4. The average recoveries for BAS 514 was 85.3% +/- 3.6 (n=6) for the shake extraction and 95.3% +/- 7.7% (n=13) for the reflux extraction. The average recoveries for BH 514-2-OH was 81.7% +/- 3.6 (n=6) for the shake extraction and 83.6% +/- 8.4% (n=13) for the reflux extraction. The average recoveries for BH 514-ME is 89.3% +/- 3.3 (n=13).

In addition to the validation run, a determination of limit of detection (LOD) and limit of quantitation (LOQ) experiment was run. The data for the worst case scenario, the reflux extraction is given. Seven

replicate fortifications were run at 10 ppb, an estimated limit of detection for the reflux method. Statistical interpretation of the method show 98% recovery of Quinclorac with a standard deviation of 8.2, n=7. As published in the article, *Principles of Environmental Analysis in Analytical Chemistry* 1983, v. 55, pgs. 2210-2218, the LOD and LOQ can be statistically determined from the data as 3 times the standard deviation and 10 times the standard deviation, respectively. A calculated LOD and LOQ for Quinclorac reflux method is 2 ppb, and 8 ppb, respectively. For BH 514-2-OH the LOD and LOQ are 1 ppb and 4 ppb respectively. The data is presented in Table 3. These calculated numbers are low limits of detection and quantitation. For purposes of this method the LOQ will be defined as what fortification level can be run successfully through the method with recoveries in the range of 70-120%. This method's quantitation limit has been shown to be 0.01 ppm.

6.0 CONCLUSION

The analytical procedure is applicable for measuring the residues of BAS 514, BH 514-2-OH and BH 514-ME in soil at levels down to 0.01 ppm. This method has been used successfully for the analysis of BAS 514, BH 514-2-OH and BH 514-ME in soil in a contract lab at levels down to 0.01 ppm.

7.0 QUALITY ASSURANCE PROCEDURES

The raw data and analytical standards of the studies referenced in this method will be stored in the BASF archives at BASF Corporation, Agricultural Products Group, 26 Davis Drive, Research Triangle Park, NC 27709-3528

8.0 REFERENCES

1. Goetz, Andrew J. "Aerobic Soil Metabolism of 14C-BAS 514 H" BASF Report M9313 July, 1993
2. Mayer, F., "HPLC Method for Determination of Quinclorac and its Metabolite BH 514-1 in Soil", BASF Method No. A8903, March 1989

9.0 SAFETY AND HEALTH CONSIDERATIONS

1. Dichloromethane is a suspected cancer agent-use with adequate ventilation, avoid breathing vapors and use it in the hood. Avoid contact with skin and eyes.
2. Methanol is extremely flammable, moderately toxic. Keep away from heat, spark, and open flame. Keep container closed. Use with adequate ventilation, avoid breathing vapors and use it in the hood.

10.0 PROTOCOL CHANGES

There were two changes to Protocol 95117. The first amendment allowed for method modifications that have been subsequently added to the method. The second amendment allowed for the addition of the analysis of BH 514-ME and the reflux analysis of BAS 514 H and BH 514-2-OH.

TABLE 1. METHOD VALIDATION DATA FOR SHAKE

Alta Sample ID	Fortification Level (ppm)	Amount Found (ppm)		Recovery (%)	
		BAS-514	BH-2-OH	BAS-514	BH-2-OH
1664_003_003FB1	NA	ND	ND	NA	NA
1664_003_003MS1	0.010	0.009	0.008	90	77
1664_003_003MS2	0.010	0.008	0.008	84	84
1664_003_003MS3	0.10	0.081	0.079	81	79
1664_003_003MS4	0.10	0.082	0.077	82	77
1664_003_003MS5	1.0	0.874	0.867	87	87
1664_003_003MS6	1.0	0.879	0.857	88	86

	Recovery (%)	
	BAS-514	BH-2-OH
Average	85.3	81.7
Std Dev (s)	3.559	4.546

TABLE 2 LOQ AND LOD DETERMINATION FOR SHAKE

ALTA Sample ID	Fortification Level (ppm)	Amount Found (ppm)		Recovery (%)	
		BAS-514	BH-2-OH	BAS-514	BH-2-OH
1664_002_0003FB1	NA	ND	ND	NA	NA
1664_002_0003MS1	0.0025	0.00247	0.00187	99	75
1664_002_0003MS2	0.0025	0.00229	0.00193	92	77
1664_002_0003MS3	0.0025	0.00248	0.00211	99	84
1664_002_0003MS4	0.0025	0.00235	0.00184	94	74
1664_002_0003MS5	0.0025	0.00249	0.00210	100	84
1664_002_0003MS6	0.0025	0.00247	0.00198	99	79
1664_002_0003MS7	0.0025	0.00244	0.00214	98	86

	Amount Found (ppm)		Recovery (%)	
	BAS-514	BH-2-OH	BAS-514	BH-2-OH
Mean	0.00243	0.00200	97	80
Std. Dev. (pop.)	7.11E-05	1.13E-04	2.81	4.45
Std. Dev.(s)	7.67E-05	1.22E-04	3.04	4.81
n	7	7	7	7
% RSD	3.2	6.1	3.1	6.0

LOD (ppm) = 3 * Std. Dev. (pop.)
 LOQ (ppm) = 10 * Std. Dev. (pop.)
 BAS-514 BH-2-OH
 LOD (ppm) = 0.000213 0.000339
 LOQ (ppm) = 0.000711 0.00113

Table 3 Method Validation Data For Reflux

ALTA ID	Spike Level ppm	BAS 514 H		514-2-OH	
		ppm	% Recovery	ppm	% Recovery
1664_008_005MS1	0.010	0.0089	89	0.008	80
1664_008_005MS2	0.010	0.0099	100	0.0076	76
1664_008_005MS3	0.010	0.0096	96	0.0085	85
1664_008_005MS4	0.010	0.0105	105	0.0076	76
1664_008_005MS5	0.010	0.0085	85	0.0086	86
1664_008_005MS6	0.010	0.0104	104	0.0084	84
1664_008_005MS7	0.010	0.0106	106	0.0084	84
1664_008_005MS8	0.040	0.0360	90	0.031	79
1664_008_005MS9	0.040	0.0377	94	0.0306	77
1664_008_005MS10	0.100	0.0892	89	0.0797	80
1664_008_005MS11	0.100	0.0906	91	0.080	80
1664_008_005MS12	1.000	1.0400	104	1.06	106
1664_008_005MS13	1.000	0.8610	86	0.94	94
Average Recovery		95.3% ± 7.7%		83.6% ± 8.4%	

LOQ and LOD Determination for Reflux (using above seven 0.01 ppm Recoveries)

	Amount Found (ppm)		Recovery (%)	
	BAS-514	BH-2-OH	BAS-514	BH-2-OH
Mean	0.0098	0.0082	98	82
Std. Dev. (pop.)	.00076	.0004	7.62	3.9
Std. Dev. (s)	.00082	.0004	8.23	4.2
n	7	7	7	7
% RSD Standard Error	8.4	4.9	8.4	5.1

LOD (ppm) = 3 * Std. Dev. (Pop.) LOD (ppm) = $\frac{\text{BAS-514}}{10}$ = .00228 LOD (ppm) = $\frac{\text{BH-2-OH}}{10}$ = .0012
 LOQ (ppm) = 10 * Std. Dev. (Pop.) LOD (ppm) = .00756 .004

TABLE 4 METHYL ESTER METHOD VALIDATION

ALTA Sample ID	Fortification Level (ppb)	Amount Found (ppb)	Recovery (%)
030196-1	Blank	NA	
030196-2	10ppb	9.072	91
030196-3	10ppb	8.524	84
030196-4	10ppb	9.08	91
030196-5	10ppb	9.036	90
030196-6	10ppb	8.676	86
030196-7	10ppb	8.496	84
030196-8	10ppb	9.092	91
030196-9	40ppb	34.856	86
030196-10	40ppb	35.12	88
030196-11	100ppb	92.54	92
030196-12	100ppb	93.164	92
030196-13	1000ppb	956.104	94
030196-14	1000ppb	922.176	92

Recovery (%)	
Average	89
Std Dev	3.3

Figure 1 Flow Chart for Quinclorac Methods

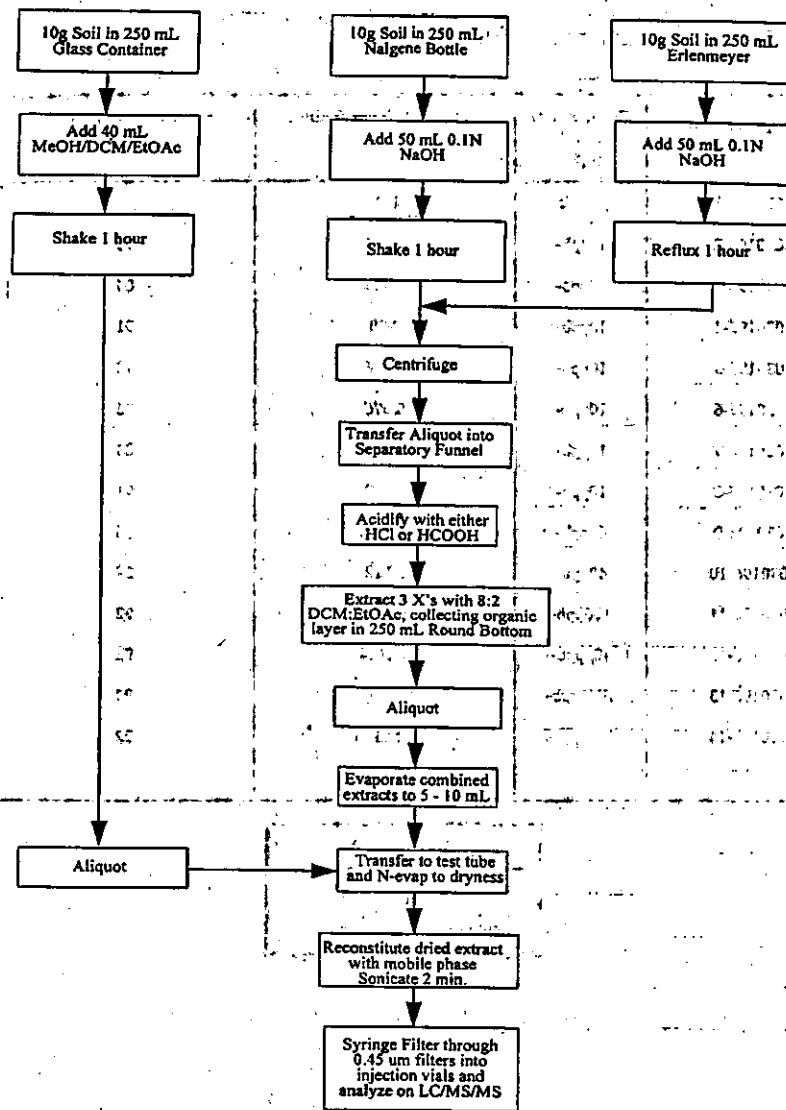
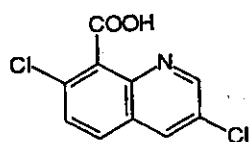
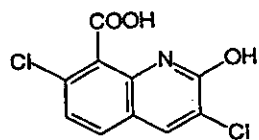


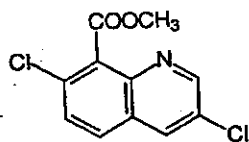
FIGURE 2 QUINCLORAC STRUCTURES



Quinclorac (BAS 514 H)



2-Hydroxyquinclorac (BH 514-2-OH)



Quinclorac methyl ester (BH 514-ME)

Figure 3

MS/MS Product Ion Spectra for Quinclorac - Negative Ion Mode

-Profile DAUGHTER, Parent = 240
Average of scans 5 to 7 Time=0.34 min
HCl Neg MSMS - 4/29/96 - 14:42
Quinclorac
2 peaks

HCl Neg MSMS/Scans 5-7

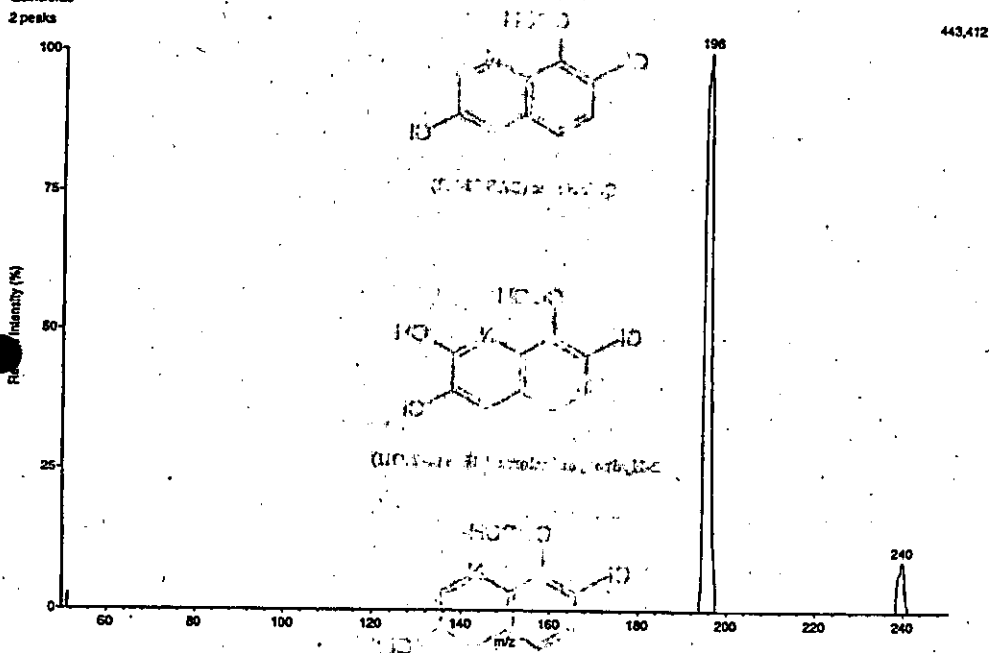


Figure 4

MS/MS Product Ion Spectra for BH 514 -2-OH - Negative Ion Mode

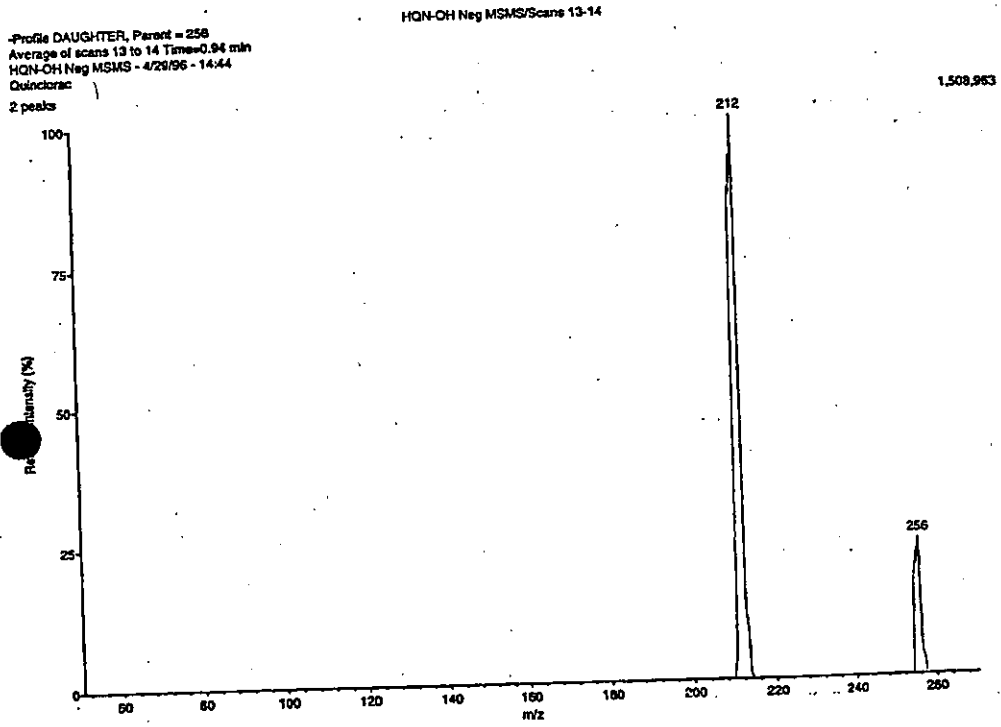


Figure 5 MS/MS Product Ion Spectra for Quinclorac - Positive Ion Mode

Profile DAUGHTER, Parent = 242
Average of scans 24 to 27 Time=0.50 min
BAS 514H Dau - 8/30/95 - 14:34
BAS 514H
5 peaks

BAS 514H Dau/Scans 24-27

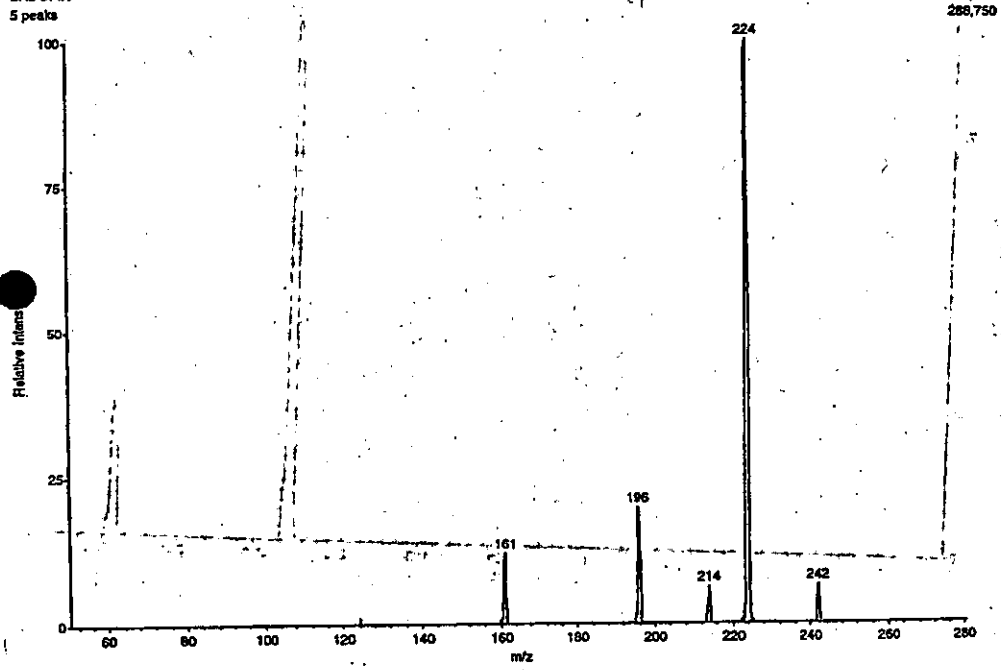


Figure 6 MS/MS Product Ion Spectra for BH 514 -2-OH - Positive Ion Mode

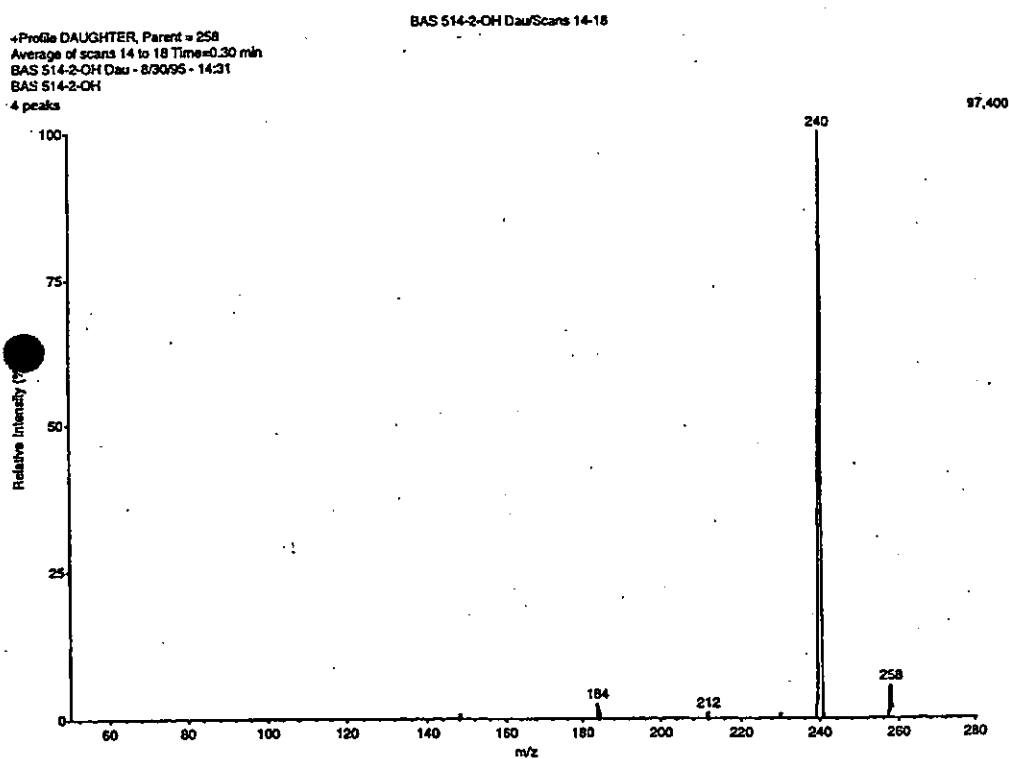
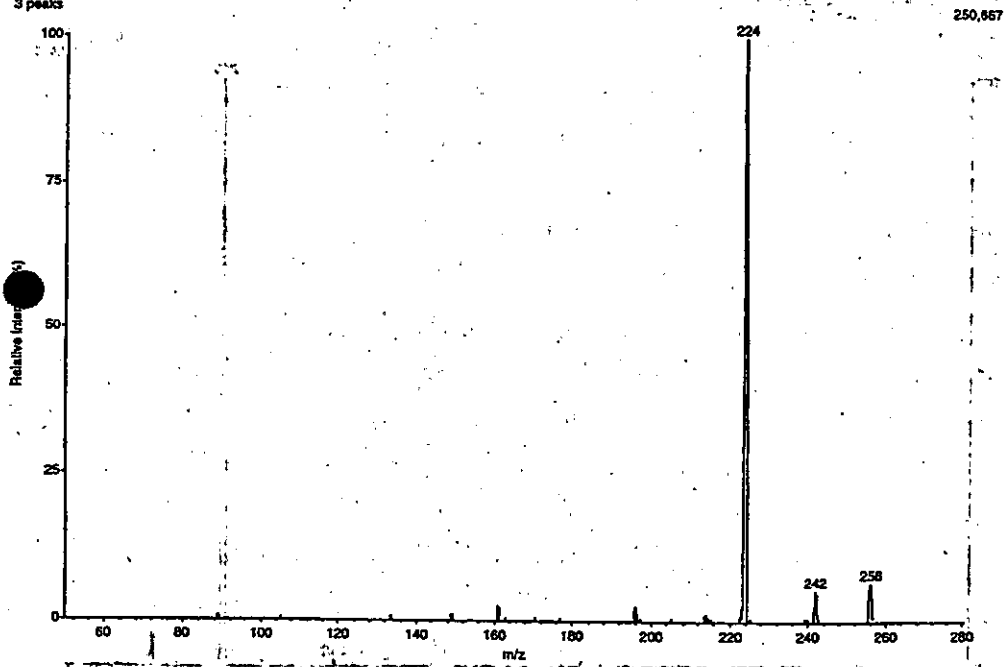


Figure 7 MS/MS Product Ion Spectra for BH 514-ME - Positive Ion Mode

-Profil DAUGHTER, Parent = 256
Average of scans 55 to 60 Time=1.15 min
BAS 514-OMe Dau - 8/30/95 - 12:36
No Title
3 peaks

BAS 514-OMe Dau/Scans 55-60



SIGNATURES

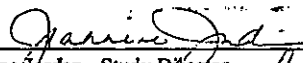
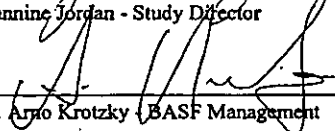
 _____ Jeannine Jordan - Study Director	<u>8/7/96</u> Date
 _____ Dr. Arno Krotzky (BASF Management)	<u>8/7/96</u> Date

Figure A - BAS 514 Quinlorac Standards (Shake Method)

Figure A-1 BAS 514 H (Quinlorac) Standard 1.25 ng/mL
Sample 951017-07
Area 985

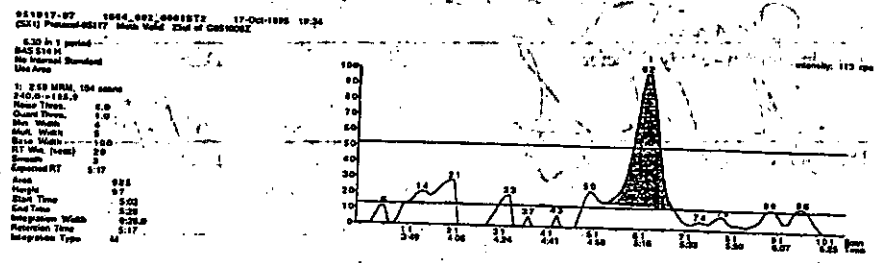


Figure A-2 BAS 514 H (Quinlorac) Standard 5.0 ng/mL
Sample 951017-11
Area 4775

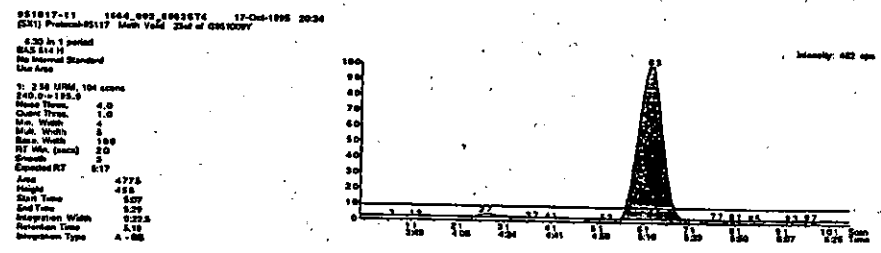


Figure A-3 BAS 514 H (Quinlorac) Standard 25.0 ng/mL
Sample 951017-15
Area 24,310

951017-15 1664_002_0002576 17-Oct-1998 21:18
[S1] Phasex-05117 Meth Vald 25.0 of 03510001
0.25 in 1 period
BAS 514 H
No Internal Standard
Use Area
1: 51 11704, 104 score
241.0-192.0
Meth Thick 4.0
Quart Thick 1.0
Min Width 4
Max Width 5
Scan Width 100
RT Min (sec) 20
Scan 2
Expected RT 0:17
Area 24310
Weight 2322
Start Time 0:05
End Time 0:20
Integration Width 0:17
Reference Time 0:17
Integration Type A - BB

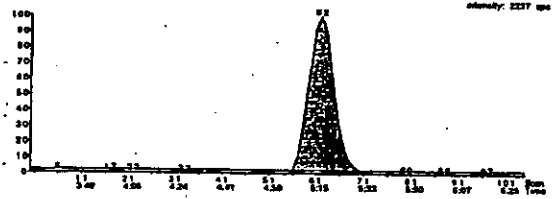
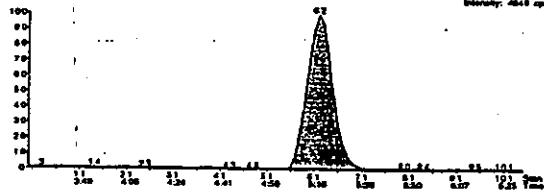


Figure A-4 BAS 514 H (Quinlorac) Standard 50.0 ng/mL
Sample 951017-19
Area 50,394

951017-19 1664_002_0002576 17-Oct-1998 22:06
[S1] Phasex-05117 Meth Vald 25.0 of 03610000
0.25 in 1 period
BAS 514 H
No Internal Standard
Use Area
1: 51 11704, 104 score
241.0-192.0
Meth Thick 4.0
Quart Thick 1.0
Min Width 4
Max Width 5
Scan Width 100
RT Min (sec) 20
Scan 2
Expected RT 0:17
Area 50394
Weight 4840
Start Time 0:05
End Time 0:20.1
Integration Width 0:17
Reference Time 0:17
Integration Type A - BB



BASF Method Number: D9513

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Figure A-5 BAS 514 H (Quinlorac) Standard 100.0 ng/mL

Sample 951017-03

Area 93,650

01/11/03 08:41:02 00000000 19-Dec-1999 16:43
(X1) Phosol 95117 10th Vial 250 of 09510000

630 in 1 vial
BAS 514 H
No Internal Standard
Use Area

1: 2.58 MIN, 93650
240.00-195.0
Name: Peak 1
Height: 4.8
Area: 93650
Max. Width: 1.8
Min. Width: 0
Base Width: 1.80
RT Min. (Sec): 2.0
Smooth: 3
Expanded RT: 1.17

Area: 93650
Height: 4.8
Start Time: 2.58
End Time: 3.58
Integration: 635.3
Retention Time: 2.57
Integration Type: A-BV

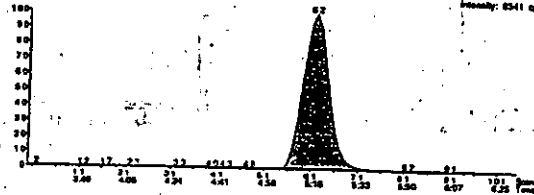


Figure B - BH 514-2-OH Standards

Figure B-1 BH 514-2-OH Standard 1.25 ng/mL
 Sample 951017-02
 Area 2,352

951017-02 1664_002_0002573 17-Oct-1995 18:31
 (E1) Protocol:95117 Meth Valid 25d of 04510257
 6.36 in 1 printed
 514-2-OH
 No Internal Standard
 Use Area
 1: 2.04 MRM, 104 score
 218.0-211.9
 Minus Thresh. 4.0
 Quant Thresh. 1.0
 Min. Width 8
 Mult. Width 8
 Ret. Width 129
 RT Min. (Secs) 3
 Smooth 3
 Expected RT 4.55
 Area 2352
 Height 291
 Start Time 4.51
 End Time 4.59
 Integration Width 0.242
 Retention Time 4.51
 Integration Type A - SB

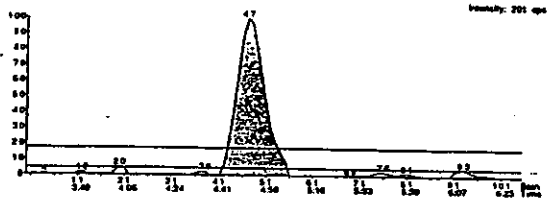
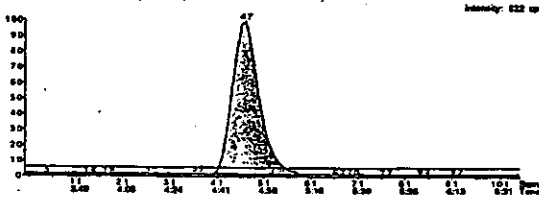


Figure B-2 BH 514-2-OH Standard 5.0 ng/mL
 Sample 951017-04
 Area 9,600

951017-04 1664_002_0002573 17-Oct-1995 16:56
 (E1) Protocol:95117 Meth Valid 25d of 04510257
 6.36 in 1 printed
 514-2-OH
 No Internal Standard
 Use Area
 1: 2.04 MRM, 104 score
 218.0-211.9
 Minus Thresh. 4.0
 Quant Thresh. 1.0
 Min. Width 8
 Mult. Width 8
 Ret. Width 129
 RT Min. (Secs) 3
 Smooth 3
 Expected RT 4.55
 Area 9600
 Height 917
 Start Time 4.53
 End Time 4.59
 Integration Width 0.242
 Retention Time 4.51
 Integration Type A - SB



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Figure B-3 BH 514-2-OH Standard 25.0 ng/mL
Sample 951017-05
Area 47,620

951017-05 1664.892.80032578 17-Oct-1995 19:00
(S/N) Protocol-05117 Meth Yield 254 of 08102002

6.20 in 1 period
814-2-OH
No Internal Standard
Use Area
1. 25.00000 100.00000
254.00-217.0
Meth Thru 4.0
Quant Thru 1.0
Min. Width 4
Max. Width 6
Base Width 100
RT (in. (sec)) 20
Smooth 3
Expected RT 4.58
Area 47620
Height 2972
Start Time 4.57
End Time 4.59
Integration Width 0.218
Retention Time 4.51
Integration Type A-99

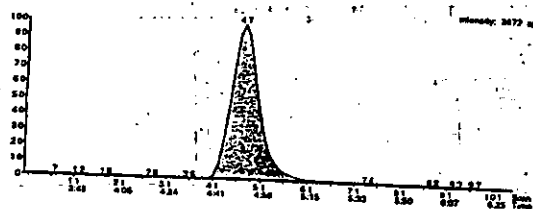


Figure B-4 BH 514-2-OH Standard 50.0 ng/mL
Sample 951017-19
Area 102,513

951017-19 1664.892.80032578 17-Oct-1995 22:00
(S/N) Protocol-05117 Meth Yield 254 of 08102002

6.20 in 1 period
814-2-OH
No Internal Standard
Use Area
1. 50.00000 100.00000
254.00-217.0
Meth Thru 4.0
Quant Thru 1.0
Min. Width 4
Max. Width 6
Base Width 100
RT (in. (sec)) 20
Smooth 3
Expected RT 4.58
Area 102513
Height 4913
Start Time 4.58
End Time 4.60
Integration Width 0.200
Retention Time 4.51
Integration Type A-99

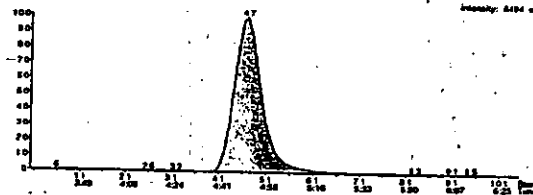


Figure B-5 BH 514-2-OH Standard 100.0 ng/mL
Sample 95101-03
Area 197,732

95101-03 1810_002_000000 11-Jun-1995 10:43
(2X1) Path=951017 Meth. Val: 25d of C619009
6.00 In 1 peak
514-2-OH
No Internal Standard
Use Area
T: 2.561996, YOH mean
256.0-257.0
Noise Thresh. 4.0
Chapt Thresh. 1.0
Min. Width 0
Max. Width 0
Band Width 1.00
RT Wtd. (area) 2.0
Smooth 3
Expected RT 4.26
Area 197732
Height 10217
Start Time 4.26
End Time 6.09
Integration Width 1.25
Retention Time 4.261
Integration Type A - 00

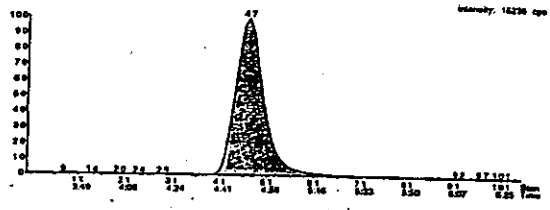


Figure C BH 514-ME (Quinclorac Methyl Ester Stds)

Figure C-1 BH 514-ME Standard 1.25 ng/mL

Sample 960304-02
Area 5,003

960304-02 STD-1.25 4-May-1996 16:00
(XX) Protocol-25117 204 of 090225A

0.20 in 1 period
SAS 514-ME
No Internal Standard
Use Area
1: 2.96 AREA, 199 counts
256.11-224.1
Height 10.0
Count Thresh. 1.0
Min. Width 0
Max. Width 0
Base Width 100
RT Min. (sec) 25
Smooth 3
Expanded RT 4.19
Area 5003
Height 4015
Start Time 3.86
End Time 4.06
Integration Width 0.20
Retention Time 4.19
Integration Type A - B

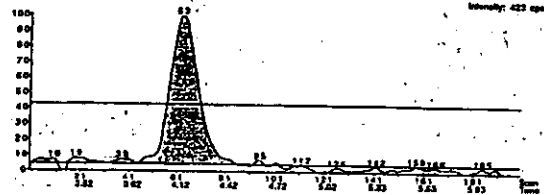


Figure C-2 BH 514-ME Standard 5.0 ng/mL

Sample 960304-10
Area 19,345

960304-10 STD-5 4-May-1996 16:00
(XX) Protocol-25117 204 of 090225A

0.20 in 1 period
SAS 514-ME
No Internal Standard
Use Area
1: 2.96 AREA, 199 counts
256.11-224.1
Height 10.0
Count Thresh. 1.0
Min. Width 0
Max. Width 0
Base Width 100
RT Min. (sec) 25
Smooth 3
Expanded RT 4.19
Area 19345
Height 16215
Start Time 3.86
End Time 4.06
Integration Width 0.20
Retention Time 4.19
Integration Type A - B

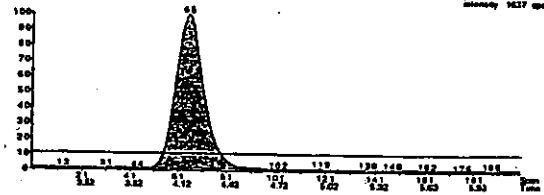


Figure C-3 BH 514-ME Standard 25.0 ng/mL
Sample 960304-07
Area 100,851

960304-07 STD-25 4-Mar-1996 16:40
(S1) Protocol:05117 2nd of C060223B
6.20 in 1 peak
BASF 514-ME
No Internal Standard
Use Area
1: 2.50 100%, 100 Areas
PSS:1-0-250.1
Peak Term: 10.0
Chart Term: 1.0
Min. Width: 0
Max. Width: 5
Base. Width: 100
RT Min. (min): 2.5
Smooth: 3
Expected RT: 4.10
Area: 100851
Height: 4200
Start Time: 3.94
End Time: 4.75
Integration Width: 0.81
Retention Time: 4.21
Integration Type: A-BV

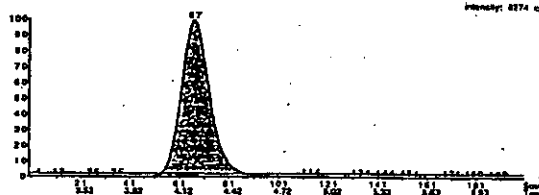
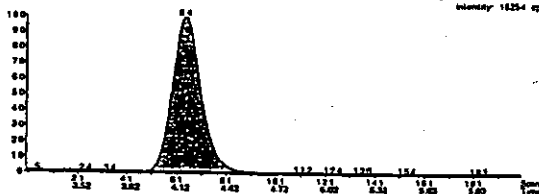


Figure C-4 BH 514-ME Standard 50.0 ng/mL
Sample 960304-04
Area 197,849

960304-04 STD-50 4-Mar-1996 16:17
(S1) Protocol:05117 2nd of C060223B
6.20 in 1 peak
BASF 514-ME
No Internal Standard
Use Area
1: 2.50 100%, 199 Areas
PSS:1-0-250.1
Peak Term: 10.0
Chart Term: 1.0
Min. Width: 0
Max. Width: 5
Base. Width: 100
RT Min. (min): 2.5
Smooth: 3
Expected RT: 4.10
Area: 197849
Height: 10200
Start Time: 3.91
End Time: 4.02
Integration Width: 0.82
Retention Time: 4.16
Integration Type: A-BV



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Figure C-5 BH 514-ME Standard 100.0 ng/mL
Sample 960304-03
Area 411,145

060304-03 STD-100 2-May-1996 10:00
(23) P:\msd001\96117 2nd of 660229

620 A 5 peaks
BAS 514-ME
No Manual Standard
Use Area

1: 2.00 LPM, 100 scans
ZSM, 1-234, 1
Inlet Temp: 10.00
Carrier Temp: 1.00
Max. Width: 5
Min. Width: 5
Scan Width: 100
RT Min. (sec): 32
Spectrum: 5
Expanded RT: 4.10

Area: 411145
Height: 33261
Start Time: 3.91
End Time: 4.08
Integration Width: 1.07
Retention Time: 4.10
Integration Type: A-BV

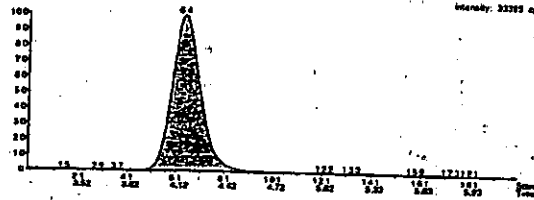


Figure D Reflux Method Standards

Figure D-1 BAS 514 Standard 5.0 ng/mL
Sample 960423-02
Area 14,396

960423-02 1664_009_0000270 23-Apr-1998 16:26
(SXI) Promont 05117 Std of CAG0025X
0.20 in 1 period
BAS 514 H
No Internal Standard
Use Area
S: 2.27 MHz, 66 scans
242.0 to 150.0
Mass Thresh. 10.0
Count Thresh. 0.5
Min. Width 5
Max. Width 5
Base. Width 100
RT Wtd. (mass) 20
Smooth 5
Expected RT 8.28
Area 14396
Height 1345
Start Time 6.13
End Time 9.06
Integration Width 0.318
Retention Time 8.27
Integration Type A - 88

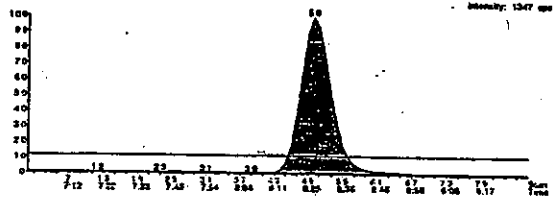


Figure D-2 BAS 514 Standard 5.0 ng/mL
Sample 960423-06
Area 56,505

960423-06 1664_009_0000270 23-Apr-1998 17:28
(SXI) Promont 05117 Std of CAG0025X
0.20 in 1 period
BAS 514 H
No Internal Standard
Use Area
S: 2.27 MHz, 66 scans
242.0 to 150.0
Mass Thresh. 10.0
Count Thresh. 0.5
Min. Width 5
Max. Width 5
Base. Width 100
RT Wtd. (mass) 20
Smooth 5
Expected RT 8.28
Area 56505
Height 5212
Start Time 6.14
End Time 9.04
Integration Width 0.318
Retention Time 8.28
Integration Type A - 88

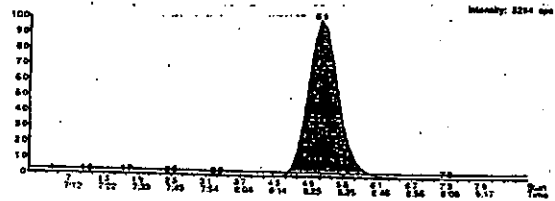
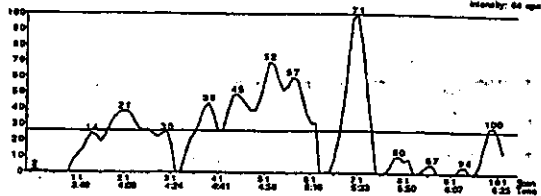


Figure E. Control Soil - Shake
Sample 951016-09

951016-09 1644_003_0001781 16-Oct-1995 16:09
(S1) Protocol: 95117 Meth Valid (E6-10/12/95) (S1M) NCM 94182-0009

0.20 In 1 ported
S1414-014
No Internal Standard
Use Area
I: 2.28 MRL 104 ppm
236.0 ± 211.3
Meth Thres. 10.0
Chanl Thres. 1.0
Min. Width 5
Max. Width 5
Base Width 128
RT Wn (sec) 25
Smooth 2
Expected RT 4.68
Area 0
Height 0
Start Time 0:00.0
End Time 0:00.0
Integration Width 0:00.0
Retention Time 0:00.0
Integration Type



951016-09 1644_003_0001781 16-Oct-1995 16:09
(S1) Protocol: 95117 Meth Valid (E6-10/12/95) (S1M) NCM 94182-0009

0.20 In 1 ported
BAS 514 H
No Internal Standard
Use Area
I: 2.28 MRL 104 ppm
240.0 ± 195.3
Meth Thres. 10.0
Chanl Thres. 1.0
Min. Width 5
Max. Width 5
Base Width 128
RT Wn (sec) 25
Smooth 2
Expected RT 5.18
Area 0
Height 0
Start Time 0:00.0
End Time 0:00.0
Integration Width 0:00.0
Retention Time 0:00.0
Integration Type

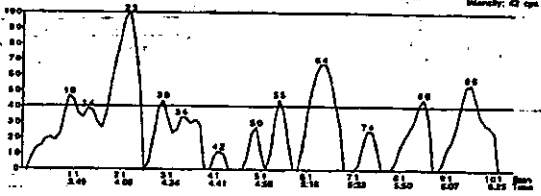
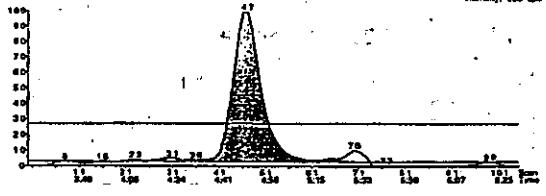


Figure F. 0.01 ppm Fortification - Shake
BAS 514 H, BH 514-2-OH
Sample 951016-10 Recovery 90%

951016-10 1644_003_0001851 16-Oct-1995 16:22
(S1) Protocol: 95117 Meth Valid (E6-10/12/95) (S1M) NCM 94182-0009

0.20 In 1 ported
S1414-014
No Internal Standard
Use Area
I: 2.28 MRL 104 ppm
236.0 ± 211.3
Meth Thres. 10.0
Chanl Thres. 1.0
Min. Width 5
Max. Width 5
Base Width 128
RT Wn (sec) 25
Smooth 2
Expected RT 4.68
Area 7247
Height 808
Start Time 4:57
End Time 5:15
Integration Width 0:26.0
Retention Time 4:51
Integration Type M



951016-10 1644_003_0001851 16-Oct-1995 16:22
(S1) Protocol: 95117 Meth Valid (E6-10/12/95) (S1M) NCM 94182-0009

0.20 In 1 ported
BAS 514 H
No Internal Standard
Use Area
I: 2.28 MRL 104 ppm
240.0 ± 195.3
Meth Thres. 10.0
Chanl Thres. 1.0
Min. Width 5
Max. Width 5
Base Width 128
RT Wn (sec) 25
Smooth 2
Expected RT 5.18
Area 3840
Height 348
Start Time 4:56
End Time 5:25
Integration Width 0:21.1
Retention Time 5:17
Integration Type M

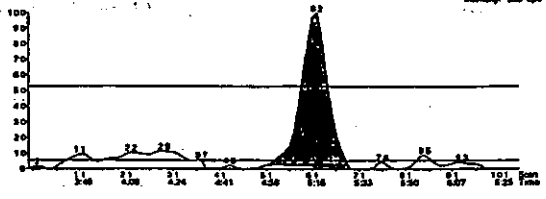
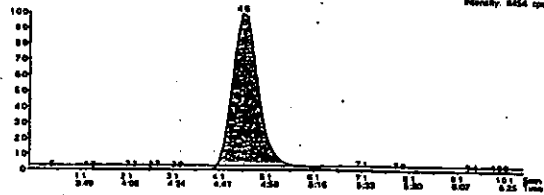


Figure G. 0.10 ppm Fortification - Shake
 BAS 514 H, BH 514-2-OH
 Sample 951016-13 Recovery 81%

951016-13 1644_009_0002M03 16-Oct-1995 17:00
 (SXI) Protocol 95117 Meth Valid (Est-101295) (q5/mL) RCM 94182-0000

0:20 in 1 period
 BAS 514 H
 No Internal Standard
 Use Area
 1: 258 MRM, 90 scans
 160.0-185.9
 Name Time: 10.0
 Count Thresh: 1.0
 Min. Width: 5
 Max. Width: 5
 RT Wd. (sec): 2.0
 Smooth: 2
 Expected RT: 4.30
 Area: 73995
 Height: 84.38
 Start Time: 4.28
 End Time: 4.32
 Integration Width: 0.484
 Retention Time: 4.30
 Integration Type: A-BV



951016-13 1644_009_0002M03 16-Oct-1995 17:00
 (SXI) Protocol 95117 Meth Valid (Est-101295) (q5/mL) RCM 94182-0000

0:20 in 1 period
 BAS 514 H
 No Internal Standard
 Use Area
 1: 258 MRM, 90 scans
 160.0-185.9
 Name Time: 10.0
 Count Thresh: 1.0
 Min. Width: 5
 Max. Width: 5
 RT Wd. (sec): 2.0
 Smooth: 2
 Expected RT: 4.30
 Area: 2276
 Height: 22.76
 Start Time: 4.28
 End Time: 4.32
 Integration Width: 0.484
 Retention Time: 4.30
 Integration Type: A-BV

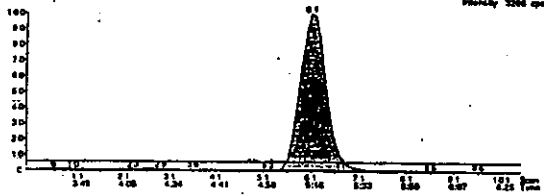
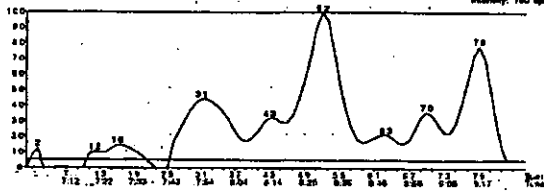


Figure H. Control Soil - Reflux
 Sample 960423-07

960423-07 1644_006_0004F01 23-Apr-1996 10:12
 (SXI) Protocol 95117 (Est-42395) RCM 94182-0057 Field Blank

0:20 in 1 period
 BAS 514 H
 No Internal Standard
 Use Area
 1: 227 MRM, 90 scans
 232.0-160.0
 Name Time: 10.0
 Count Thresh: 0.5
 Min. Width: 5
 Max. Width: 5
 RT Wd. (sec): 2.0
 Smooth: 2
 Expected RT: 7.51
 Area: 0
 Height: 0
 Start Time: 0:00.0
 End Time: 0:00.0
 Integration Width: 0:00.0
 Retention Time: 0:00.0
 Integration Type:



960423-07 1644_006_0004F01 23-Apr-1996 10:12
 (SXI) Protocol 95117 (Est-42395) RCM 94182-0057 Field Blank

0:20 in 1 period
 BAS 514 H
 No Internal Standard
 Use Area
 1: 227 MRM, 90 scans
 232.0-160.0
 Name Time: 10.0
 Count Thresh: 0.5
 Min. Width: 5
 Max. Width: 5
 RT Wd. (sec): 2.0
 Smooth: 2
 Expected RT: 7.51
 Area: 0
 Height: 0
 Start Time: 0:00.0
 End Time: 0:00.0
 Integration Width: 0:00.0
 Retention Time: 0:00.0
 Integration Type:

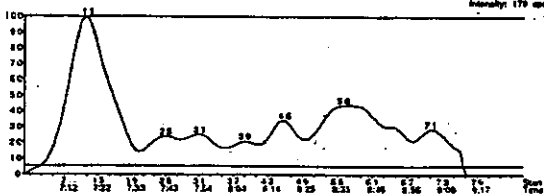


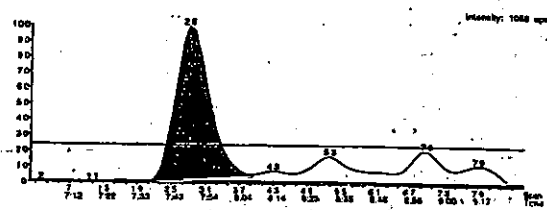
Figure I. 0.01 ppm Fortification Reflux
BAS 514, BH 514-2-OH
Sample 960423-08 Recovery 89%, 84%

960423-08 1064 006 0006M51 23-Apr-1998 01:23
 (S1) Protocol 03117 (S1-4/23/98) RCM 04182-0037 100 ppb MS

0.29 in 1 peak
 514-2-OH
 No Internal Standard
 Use Area

1: 2.27 AREA, 86 score
 258.0-163.3
 Clump Thres. 10.0
 Min. Width 5
 Max. Width 5
 Base Width 100
 RT Min. (sec) 20
 Smooth 5
 Expected RT 7.51

Area 19209
 Height 1034
 Start Time 7.28
 End Time 7.28
 Integration Width 0.254
 Retention Time 7.51
 Integration Type M



960423-08 1064 006 0006M51 23-Apr-1998 01:29
 (S1) Protocol 03117 (S1-4/23/98) RCM 04182-0037 100 ppb MS

0.29 in 1 peak
 BAS 514 H
 No Internal Standard
 Use Area

1: 2.27 AREA, 86 score
 242.0-160.8
 Clump Thres. 10.0
 Min. Width 5.5
 Max. Width 5
 Base Width 100
 RT Min. (sec) 18
 Smooth 5
 Expected RT 8.26

Area 23221
 Height 2364
 Start Time 8.24
 End Time 8.24
 Integration Width 0.450
 Retention Time 8.20
 Integration Type M

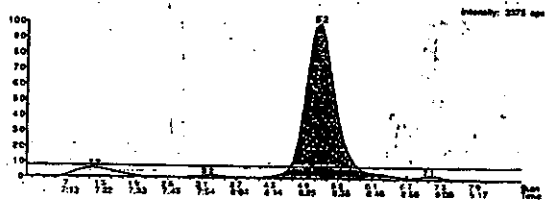


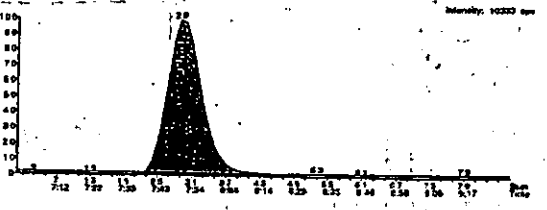
Figure J. 0.10 ppm Fortification Reflux
BAS 514, BH 514-2-OH
Sample 960423-20 Recovery 89%, 80%

960423-20 1064 006 0006M51 23-Apr-1998 01:26
 (S1) Protocol 03117 (S1-4/23/98) RCM 04182-0037 100 ppb MS

0.29 in 1 peak
 514-2-OH
 No Internal Standard
 Use Area

1: 2.27 AREA, 86 score
 258.0-163.3
 Clump Thres. 10.0
 Min. Width 5
 Max. Width 5
 Base Width 100
 RT Min. (sec) 20
 Smooth 5
 Expected RT 7.51

Area 198328
 Height 10338
 Start Time 7.28
 End Time 7.28
 Integration Width 0.254
 Retention Time 7.50
 Integration Type A-SV



960423-20 1064 006 0006M51 23-Apr-1998 01:26
 (S1) Protocol 03117 (S1-4/23/98) RCM 04182-0037 100 ppb MS

0.29 in 1 peak
 BAS 514 H
 No Internal Standard
 Use Area

1: 2.27 AREA, 86 score
 242.0-160.8
 Clump Thres. 10.0
 Min. Width 5.5
 Max. Width 5
 Base Width 100
 RT Min. (sec) 18
 Smooth 5
 Expected RT 8.26

Area 257001
 Height 25703
 Start Time 8.07
 End Time 8.07
 Integration Width 1.16
 Retention Time 8.20
 Integration Type A-SV

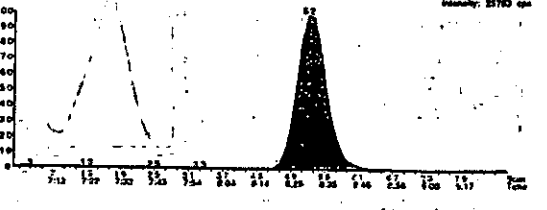


Figure K. Control Soil - BH 514-ME
Sample 0301-96-1

000004-05 030196-1 4-Mar-1996 10:25
(SXI) Protocol-95117 Field Blank
6.20 in 1 packet
BAG 514-ME
No Internal Standard
Use Area
1: 2.00 MS94, 100 atoms
254.1=224.1
Peak Time: 10.0
Count Time: 1.0
Min. Width: 5
Max. Width: 5
Base Width: 100
RT Min. (sec): 25
Smooth: 3
Expected RT: 4.19
Area: 0
Height: 0
Start Time: 0.00
End Time: 0.00
Integration Width: 0.00
Reference Time: 0.00
Integration Type:

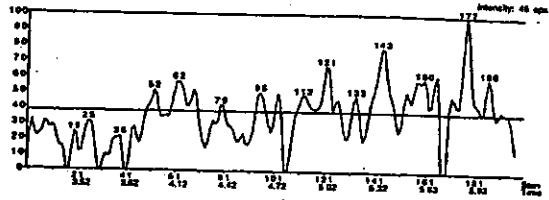


Figure L. 0.01 ppm Fortification - BH 514-ME
Sample 030196-2 Recovery 91%

000004-05 030196-2 4-Mar-1996 10:35
(SXI) Protocol-95117 10 ppm MS1
6.20 in 1 packet
BAG 514-ME
No Internal Standard
Use Area
1: 2.00 MS94, 100 atoms
254.1=224.1
Peak Time: 10.0
Count Time: 1.0
Min. Width: 5
Max. Width: 5
Base Width: 100
RT Min. (sec): 25
Smooth: 3
Expected RT: 4.19
Area: 6076
Height: 751
Start Time: 8.82
End Time: 4.33
Integration Width: 0.00
Reference Time: 4.18
Integration Type: A-SB

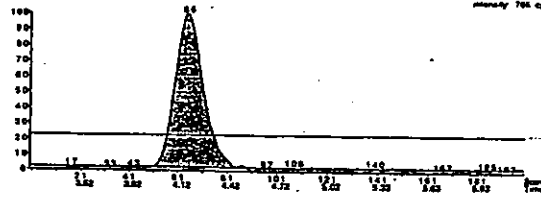


Figure M. 0.10 ppm Fortification
Sample 030196-11 Recovery 92%

030196-11 030196-11 4-Mar-1996 20:21
GC13) Method:05117 500 ppb L251 #2
2.50 in 1 period
BAG 514-44z
No Internal Standard
Chir Name
1: 2.99 100% 100 amount
256.1-224.1
Pulse Time: 10.00
Chart Type: 1.0
Min. Width: 1.0
Max. Width: 100.0
RT Min. (Sec): 35
Spectrum RT: 4.10
Area: 47742
Height: 3878
Start Time: 3.94
End Time: 4.20
Integration Width: 0.26
Integration Time: 4.21
Integration Type: A - BY

