

Cover Sheet for

**ENVIRONMENTAL CHEMISTRY METHOD**

***Pesticide Name:*** Quinclorac

***MRID #:*** 440866-01

***Matrix:*** Soil

***Analysis:*** LC/MS/MS

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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.

## 1.2 REFERENCE SUBSTANCES

|                       |   |                |                         |
|-----------------------|---|----------------|-------------------------|
| Common Name:          | Quinclorac  |                |                         |
| BASF Code:            | BAS 514 H   |                |                         |
| Chemical Name:        | 3,7-dichloro-8-quinolinecarboxylic acid           |                |                         |
| Empirical Formula:    | $C_{10}H_6Cl_2N_2O_2$                             |                |                         |
| Molecular Weight:     | 242   |                |                         |
| Melting Point:        | Above 237°C                                       |                |                         |
| Appearance:           | White, Solid                                      |                |                         |
| Odor:                 | Odorless  |                |                         |
| Solubility - at 20°C: | (g/100 g solvent, 20°C)                           |                |                         |
| Water:                | $6.2 \times 10^{-3}$                              | 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 Soluble |
| Ethanol:              | 0.2   |                |                         |
| Common Name:          | 2-HydroxyQuinclorac                               |                |                         |
| BASF Code:            | BH 514-2-OH                                       |                |                         |
| Chemical Name:        | 3,7-dichloro-2-hydroxy-8-quinolinecarboxylic acid |                |                         |
| Empirical Formula:    | $C_{10}H_6Cl_2N_2O_3$                             |                |                         |
| Molecular Weight:     | 258   |                |                         |
| Common Name:          | Quinclorac methyl ester                           |                |                         |
| BASF Code:            | BH 514-ME   |                |                         |
| Chemical Name:        | 3,7-dichloro-2-hydroxy-8-quinolinecarboxylate     |                |                         |
| Empirical Formula:    | $C_{11}H_6Cl_2N_2O_2$                             |                |                         |
| Molecular Weight:     | 256   |                |                         |

## 1.3 PRINCIPLE OF THE METHOD

For BAS 514 H (Quinclorac) 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 quantization for each metabolite is 0.01 ppm.

**2.0 MATERIALS AND METHODS****2.1 Equipment**

Rotary evaporator:

N-Evap (Nitrogen Stream

Centrifuge:

Mechanical shaker:

Mini Centrifuge:

Centrifuge filter for mini-centrifuge:

Separatory funnels:

Flat bottom flasks:

Centrifuge glass tubes with  
teflon lined screw top flasks

Glass Bottles

Volumetric flasks:

Volumetric pipettes:

Graduate pipettes:

Long stem funnels:

Conical inserts:

Autosampler vials:

Phase Separator Paper:

Magnetic stirring bars

Reflux condenser

Stirring hot plate

Ultrasonic Bath

Top loading balance

Other general laboratory glassware and supplies.

**Suggested Sizes/Manufacturers**

Buchi Rotovapov or equivalent

Organization Assoc. or equivalent

IPC PR 700 Refrigerated or  
Equivalent

Janke &amp; Kunzel HS 501D

Capitate HF-120 Millipore or  
equivalent 1.5ml/0.45  
micron nylon

MSI or equivalent

250 mL, 125 mL

300 mL

50 Fisher Scientific

50 mL

10, 25, 50, 100 mL

0.5, 1, 5, 10, 25 mL

1 mL

75 mm id

200 µL Varian or equivalent

1.5 mL Varian or equivalent

15.0 cm I PS

2.5 cm

Standard joint

Corning PC-351

Branson 1200

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/Preparation

Baxter Healthcare Corporation, B&J Brand  
CAS 75-09-2

Baxter Healthcare Corporation, B&J Brand  
CAS 67-56-1

Baxter Healthcare Corporation, B&J Brand  
CAS 67-56-1

Baxter Healthcare Corporation, B&J Brand  
CAS 7732-18-5

Baxter Healthcare Corporation, B&J Brand  
CAS 111-90-0

Aldrich Chemical cat#10,652-6  
CAS 64-18-6

Aldrich Chemical cat#25,814-8,  
CAS 7647-01-0

Aldrich Chemical cat#15,626-4  
CAS 540-69-2

Aldrich Chemical cat#37,233-1  
CAS 631-61-8

Aldrich Chemical cat#31,951-1  
CAS 1310-73-2

2.3 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-Z-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/water 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 portions. Rinse the phase separation paper with the methylene chloride:ethyl acetate solvent, and add the rinses 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°±5°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°±5°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°±5°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°±5°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/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 µL conical insert into a 1.5 mL glass auto sampler vial. Transfer the filtered solution into the 200 µL 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 $\pm$ 5 $^{\circ}$ 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 Quincloric and 7-OH-Quincloric 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:** 0.1% formic acid

**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  $\mu$ L

*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.*

|                       |                        |
|-----------------------|------------------------|
| <b>Mode:</b>          | Negative Ion Ion Spray |
| <b>ISV Voltage:</b>   | -3 kV                  |
| <b>Orifice:</b>       | -56 V                  |
| <b>Curtain Gas:</b>   | Nitrogen @ 1L/min      |
| <b>Nebulizer Gas:</b> | Nitrogen @ 80 psi      |
| <b>Auxiliary Gas:</b> | Nitrogen @ 1L/min      |

Interface Setpoint: 65°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 Quinelorac and 2-OH-Quinelorac 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: 0.1% formic acid  
 Mobile Phase B: Methanol with 0.1% formic acid and 5 mM ammonium acetate  
 Flow Rate: 0.3 mL/min with ~1:13 post-column split (Valco ecc 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 TurboIonSpray  
 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 | 238/184                      | 7:55                    |

**Analysis of Quinolorge Methyl Ester****HPLC Operating Conditions:**

Column: Betasil C18, 100 x 2 mm, P/N 105-701-2-CFF, Keystone Scientific, State College, PA (814) 353-2300  
 Guard Column: Betasil, 20 x 2 mm Javelin, P/N 88202-701-P  
 Mobile Phase A: 0.1% formic acid  
 Mobile Phase B: Methanol with 0.1% formic acid  
 Flow Rate: 0.4 mL/min with ~1:10 post-column split (Value too 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 Ion Spray  
 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 eV  
 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  
 Scaling Mass: 100

| Analyte    | Precursor/Product Ions<br>(m/z) | Retention Time<br>(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 quantization 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 1mm from the end. Connect the column to the Tee using a short piece of 0.007" tubing. Connect a 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" peak 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 = mg Sample injected =  $\frac{\text{sample wt. (g)} \times \mu\text{l injected}}{\text{Final dilution volume (mL)}}$

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:

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

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).



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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.

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BEC 43310 PG 00268

**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              | 0.007   | 90           | 77      |
| 1664_003_003MS2 | 0.010                     | 0.008              | 0.008   | 84           | 84      |
| 1664_003_003MS3 | 0.10                      | 0.081              | 0.078   | 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) | 3.359        | 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_001_0001FB1 | NA                        | ND                 | ND      | NA           | NA      |
| 1664_001_0001MS1 | 0.0025                    | 0.00247            | 0.00187 | 99           | 73      |
| 1664_001_0001MS2 | 0.0025                    | 0.00229            | 0.00193 | 92           | 77      |
| 1664_001_0001MS3 | 0.0025                    | 0.00248            | 0.00211 | 99           | 84      |
| 1664_001_0001MS4 | 0.0025                    | 0.00235            | 0.00184 | 94           | 74      |
| 1664_001_0001MS5 | 0.0025                    | 0.00249            | 0.00210 | 100          | 84      |
| 1664_001_0001MS6 | 0.0025                    | 0.00247            | 0.00198 | 99           | 79      |
| 1664_001_0001MS7 | 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<br>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              | 0.0103    | 103        | 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              | 0.0370    | 94         | 0.0306   | 77         |
| 1664_008_005MS10 | 0.100              | 0.0890    | 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         |

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.)  
 LOQ (ppm) = 10 \* Std. Dev. (Pop.)

BAS-514      BH-2-OH  
 LOD (ppm) = .00228      .0012  
 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      | 89.8 |
| Std Dev      | 3.3  |

Figure 1

Flow Chart for Quinclorac Methods

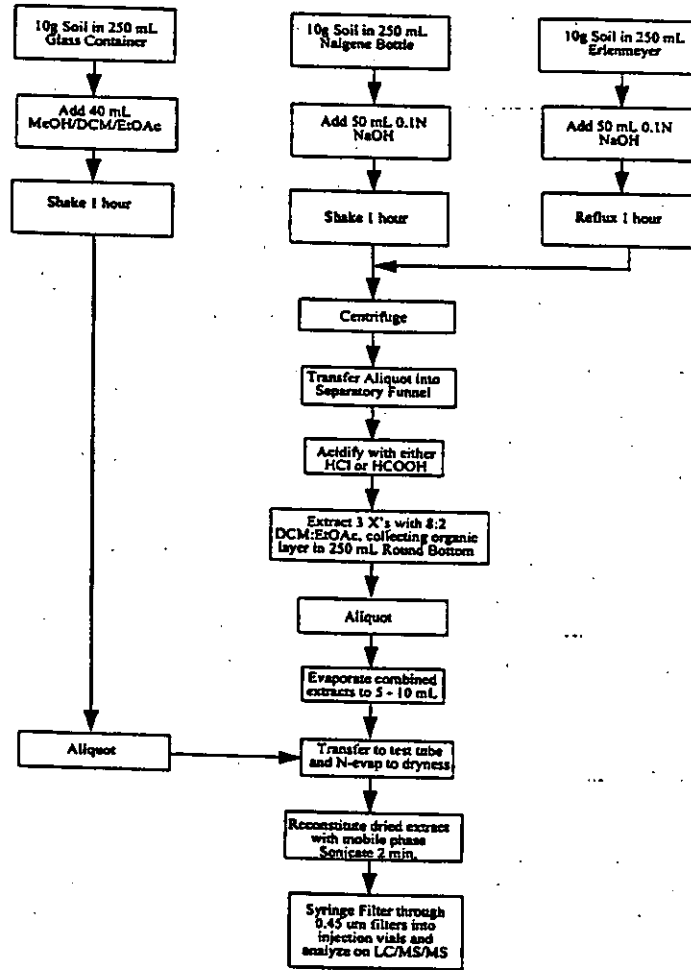
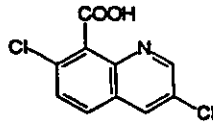
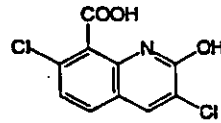


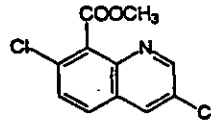
FIGURE 2 QUINCLORAC STRUCTURES



Quinclorac (BAS 514 H)

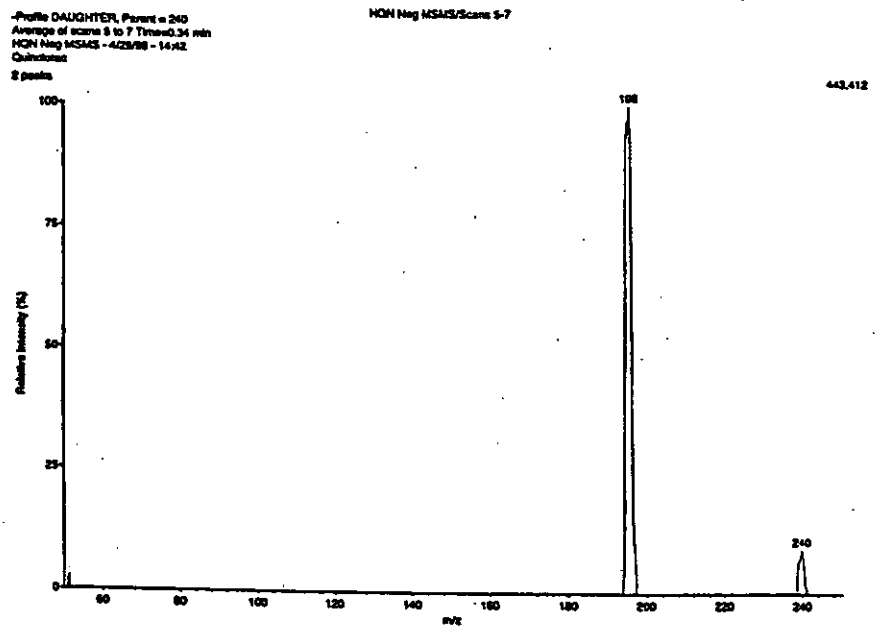


2-Hydroxyquinclorac (BH 514-2-OH)



Quinclorac methyl ester (BH 514-ME)

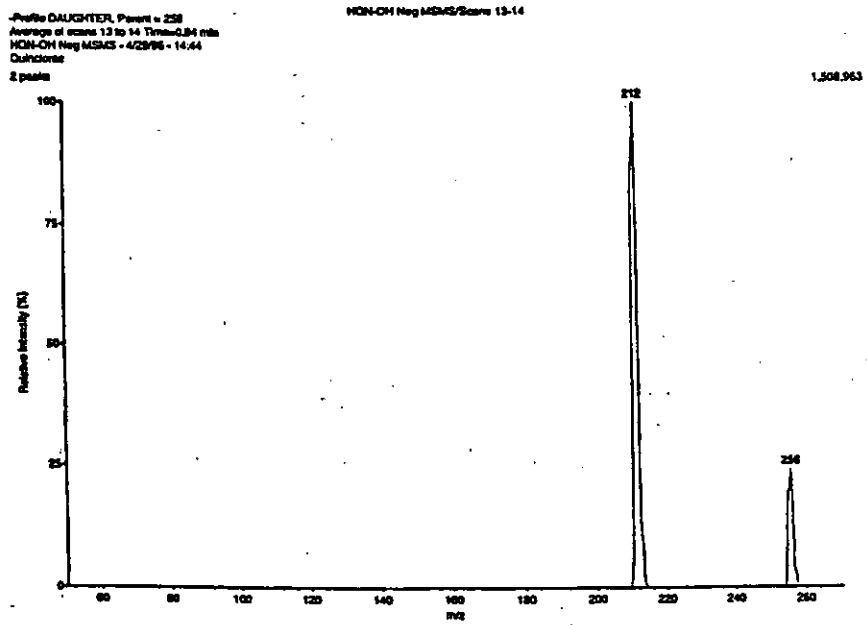
Figure 3 MS/MS Product Ion Spectra for Quinclorac - Negative Ion Mode



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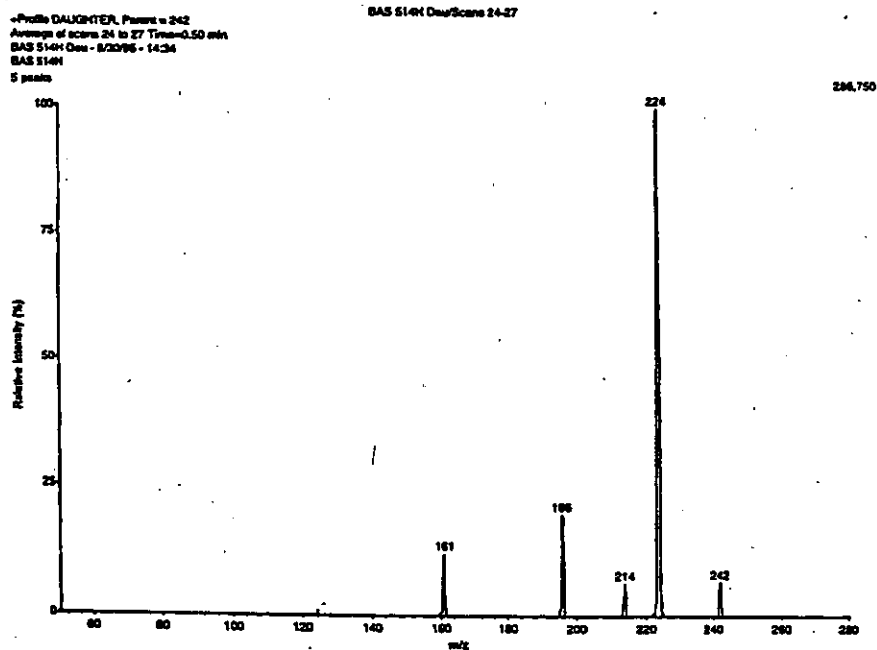


Figure 4 MS/MS Product Ion Spectra for BH 514 -2-OH - Negative Ion Mode



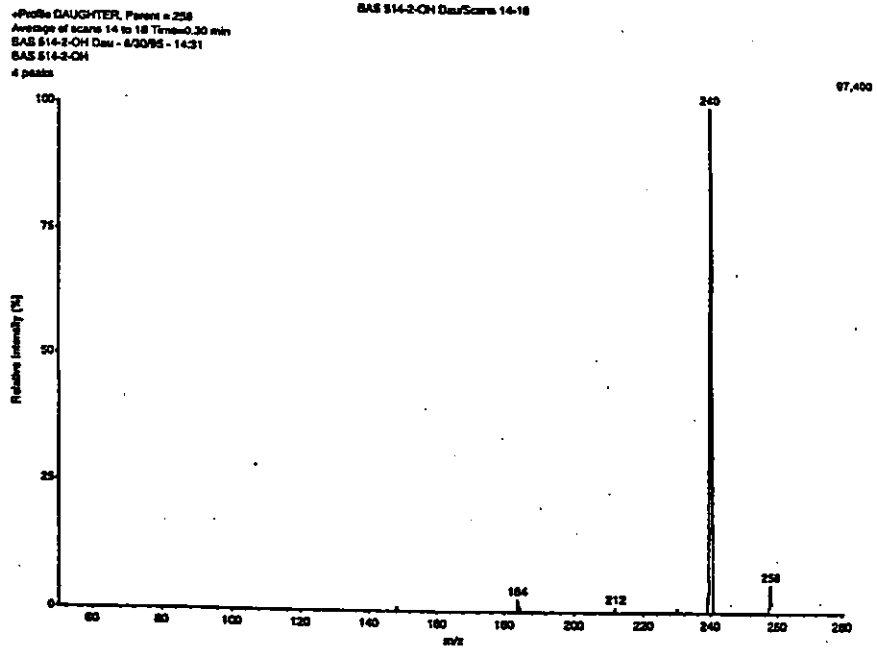
G:\JORDAN\SI\METH1.DOC

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



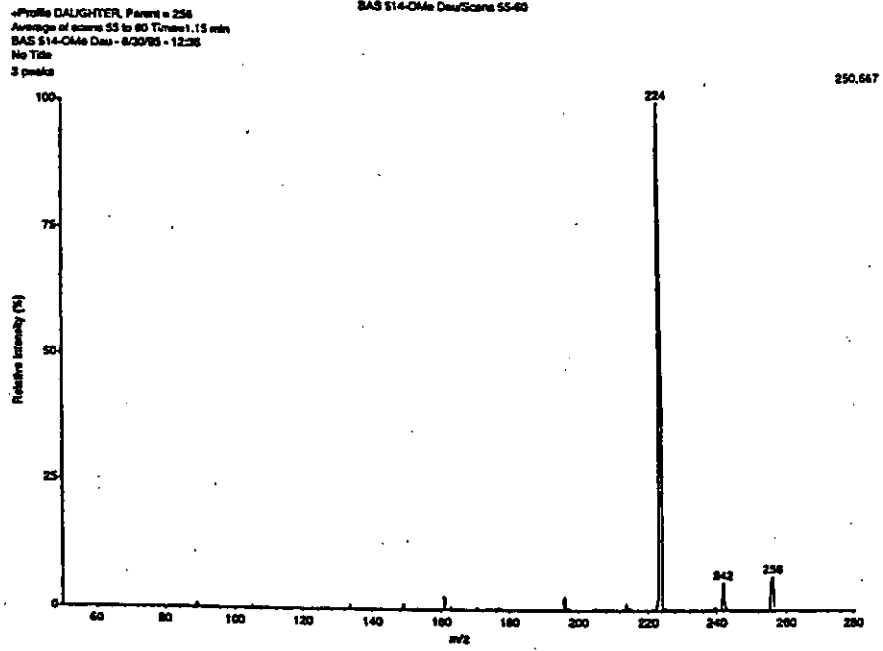
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Figure 6 MS/MS Product Ion Spectra for BH 514 :2-OH - Positive Ion Mode



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



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Appendix - Typical Chromatograms

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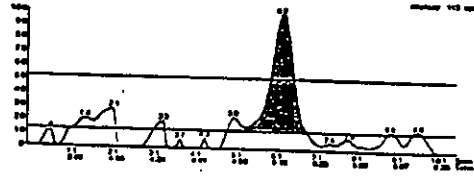
ABC 43318 PG 88088

BASF Method Number: D9513

**Figure A - BAS 514 Quinclorac Standards (Shake Method)**

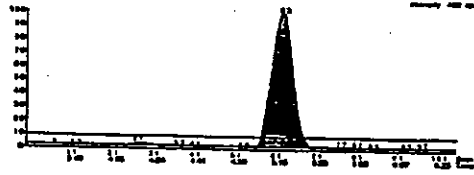
**Figure A-1 BAS 514 H (Quinclorac) Standard 1.23 ng/mL**  
Sample 951017-07  
Area 985

```
951017-07 1480_000_000000 17-06-1999 10:30
951017-07
INSTRUMENT: 6890
METHOD: 951017-07
SAMPLE: 951017-07
CONCENTRATION: 1.23
INTEGRATION: 1.23
PEAKS: 1
AREA: 985
AREA%: 100
START TIME: 0.10
STOP TIME: 12.00
SAMPLING RATE: 0.50
```



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

```
951017-11 1480_000_000000 17-06-1999 10:30
951017-11
INSTRUMENT: 6890
METHOD: 951017-07
SAMPLE: 951017-11
CONCENTRATION: 5.0
INTEGRATION: 5.0
PEAKS: 1
AREA: 4775
AREA%: 100
START TIME: 0.10
STOP TIME: 12.00
SAMPLING RATE: 0.50
```



BASF Method Number: D9513

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

```
05/10/17 16:00:00 3000,000,30000000 17.00-18.00 01:16
051017-15 15.0000000000 15.0000000000
051017-15 15.0000000000 15.0000000000
051017-15 15.0000000000 15.0000000000
051017-15 15.0000000000 15.0000000000
051017-15 15.0000000000 15.0000000000
051017-15 15.0000000000 15.0000000000
051017-15 15.0000000000 15.0000000000
051017-15 15.0000000000 15.0000000000
051017-15 15.0000000000 15.0000000000
051017-15 15.0000000000 15.0000000000
```

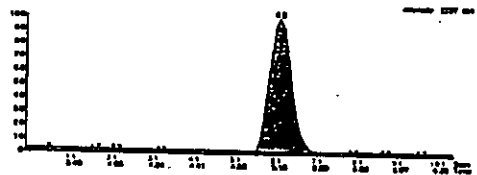
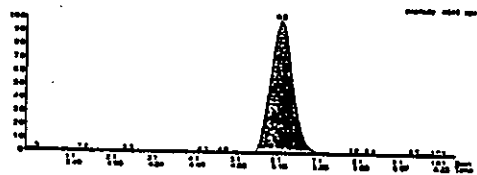


Figure A-4 BAS 514 H (Quinolone) Standard 50.0 ng/mL  
 Sample 951017-19  
 Area 50,394

```
05/10/17 16:00:00 3000,000,30000000 17.00-18.00 02:00
051017-19 15.0000000000 15.0000000000
051017-19 15.0000000000 15.0000000000
051017-19 15.0000000000 15.0000000000
051017-19 15.0000000000 15.0000000000
051017-19 15.0000000000 15.0000000000
051017-19 15.0000000000 15.0000000000
051017-19 15.0000000000 15.0000000000
051017-19 15.0000000000 15.0000000000
051017-19 15.0000000000 15.0000000000
051017-19 15.0000000000 15.0000000000
```



BASF Method Number: D9513

Figure A-5 BAS 514 H (Quinolrac) Standard 100.0 ng/mL  
Sample 951017-03  
Area 93.650

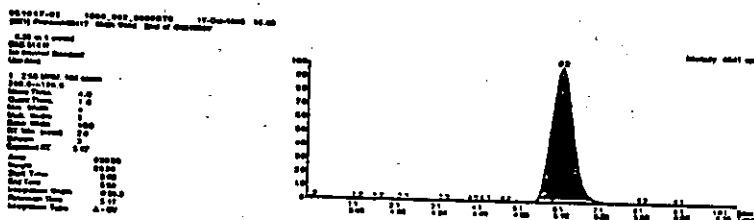




Figure B - BH 514-2-OH Standards

Figure B-1 BH 514-2-OH Standard 1.25 ng/mL  
Sample 931017-02  
Area 2,332

931017-02 1000\_002\_0000071 17-08-1998 10:30  
0.20 µL Inj  
514-2-OH  
BH 514-2-OH Standard  
1.25 ng/mL  
1. 2.500000 1000000  
Peak Name: 1.0  
Retention Time: 4.30  
Area: 2332  
Height: 100  
Width: 0.20  
Height at Peak: 100  
Area Under Peak: 2332  
Area Percent: 100  
Sample Name: 931017-02  
Injection Volume: 0.20  
Injection Speed: 200  
Injection Temperature: 200  
Injection Time: 4.30

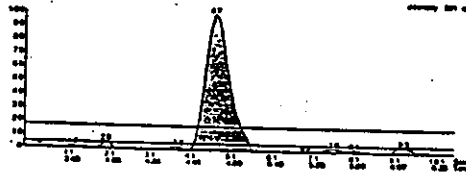
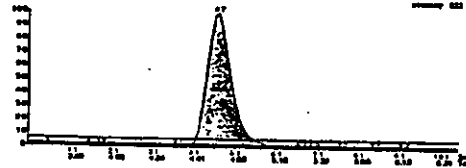


Figure B-2 BH 514-2-OH Standard 5.0 ng/mL  
Sample 931017-04  
Area 9,600

931017-04 1000\_002\_0000070 17-08-1998 10:30  
0.20 µL Inj  
514-2-OH  
BH 514-2-OH Standard  
5.0 ng/mL  
1. 5.000000 1000000  
Peak Name: 1.0  
Retention Time: 4.30  
Area: 9600  
Height: 100  
Width: 0.20  
Height at Peak: 100  
Area Under Peak: 9600  
Area Percent: 100  
Sample Name: 931017-04  
Injection Volume: 0.20  
Injection Speed: 200  
Injection Temperature: 200  
Injection Time: 4.30









BASF Method Number: D9513

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

00000007 070-00 20000000 10.00  
[Data Parameters] [End of Spectrum]  
0.20 to 1.0000  
[Data Parameters] [End of Spectrum]  
1. 2.00 0.000 100.0000  
200.00 1.0000  
Area: 100.851  
Peak: 100.851  
Height: 100.851  
Width: 1.0000  
Retention Time: 1.0000  
Integration Type: A-B

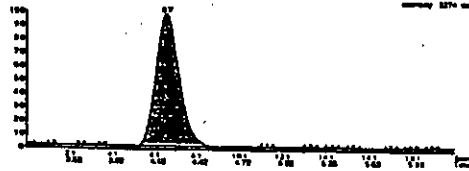


Figure C-4 BH 514-ME Standard 50.0 ng/mL  
Sample 960304-04  
Area 197,849

00000004 070-00 20000000 10.00  
[Data Parameters] [End of Spectrum]  
0.20 to 1.0000  
[Data Parameters] [End of Spectrum]  
1. 2.00 0.000 100.0000  
200.00 1.0000  
Area: 197.849  
Peak: 197.849  
Height: 197.849  
Width: 1.0000  
Retention Time: 1.0000  
Integration Type: A-B

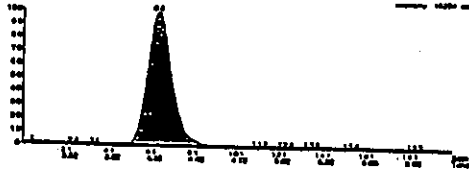


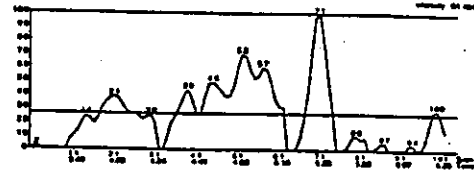




Figure E. Control Soil - Shake  
Sample 951016-09

021016-09 1000\_000\_00000015 10-08-2001 00 20  
021016-09 1000\_000\_00000015 10-08-2001 00 20

0.20 mL Injected  
0.20 mL Sample  
0.20 mL Standard  
0.20 mL Matrix  
0.20 mL Dilution  
0.20 mL Elution  
0.20 mL Clean-up  
0.20 mL Reagent  
0.20 mL Solvent  
0.20 mL Carrier  
0.20 mL Internal Standard  
0.20 mL Spike  
0.20 mL Blank  
0.20 mL Reagent  
0.20 mL Solvent  
0.20 mL Carrier  
0.20 mL Internal Standard  
0.20 mL Spike  
0.20 mL Blank



021016-09 1000\_000\_00000015 10-08-2001 00 20  
021016-09 1000\_000\_00000015 10-08-2001 00 20

0.20 mL Injected  
0.20 mL Sample  
0.20 mL Standard  
0.20 mL Matrix  
0.20 mL Dilution  
0.20 mL Elution  
0.20 mL Clean-up  
0.20 mL Reagent  
0.20 mL Solvent  
0.20 mL Carrier  
0.20 mL Internal Standard  
0.20 mL Spike  
0.20 mL Blank

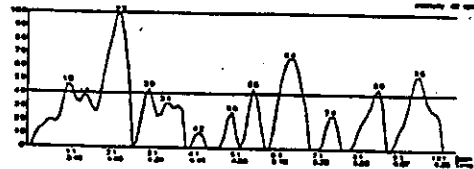
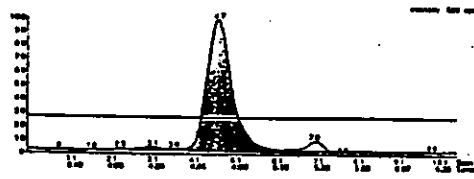


Figure F. 0.01 ppm Fortification - Shake  
BAS 514 H, BH 514-2-OK  
Sample 951016-10 Recovery 90%

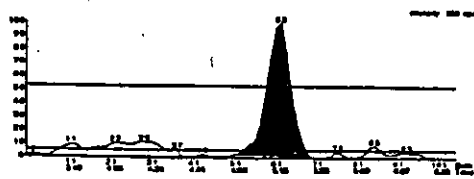
021016-10 1000\_000\_00000015 10-08-2001 00 20  
021016-10 1000\_000\_00000015 10-08-2001 00 20

0.20 mL Injected  
0.20 mL Sample  
0.20 mL Standard  
0.20 mL Matrix  
0.20 mL Dilution  
0.20 mL Elution  
0.20 mL Clean-up  
0.20 mL Reagent  
0.20 mL Solvent  
0.20 mL Carrier  
0.20 mL Internal Standard  
0.20 mL Spike  
0.20 mL Blank



021016-10 1000\_000\_00000015 10-08-2001 00 20  
021016-10 1000\_000\_00000015 10-08-2001 00 20

0.20 mL Injected  
0.20 mL Sample  
0.20 mL Standard  
0.20 mL Matrix  
0.20 mL Dilution  
0.20 mL Elution  
0.20 mL Clean-up  
0.20 mL Reagent  
0.20 mL Solvent  
0.20 mL Carrier  
0.20 mL Internal Standard  
0.20 mL Spike  
0.20 mL Blank





BASF Method Number: D9513

Figure G. 0.10 ppm Fortification - Shake  
BAS S14 H, BH S14-2-OH  
Sample 951016-13 Recovery 81%

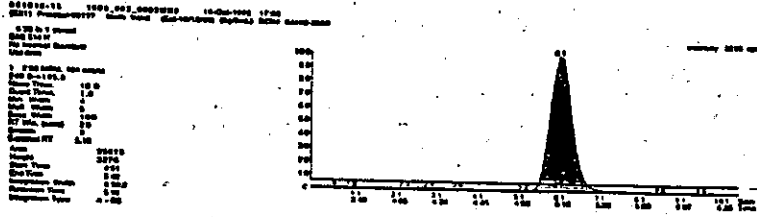
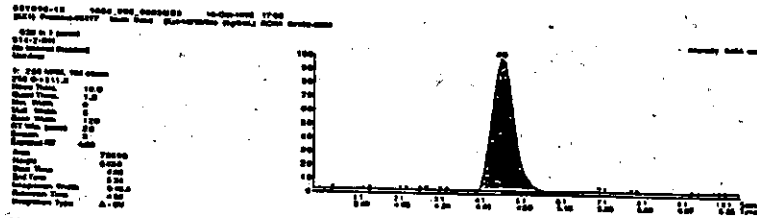
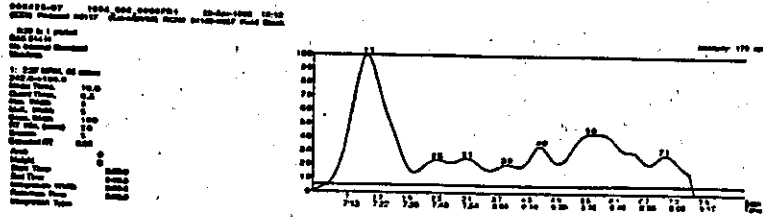
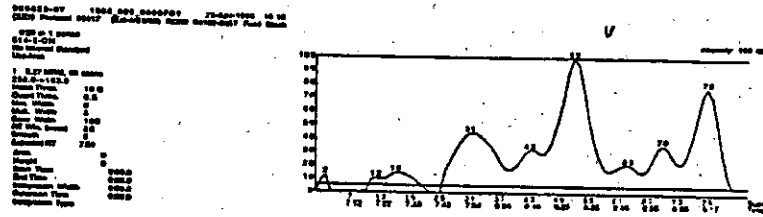


Figure H. Control Soil - Reflux  
Sample 960423-07



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Figure I. 0.01 ppm Fortification Reflux  
BAS 514, BH 514-2-OH  
Sample 960423-02 Recovery 89%, 84%

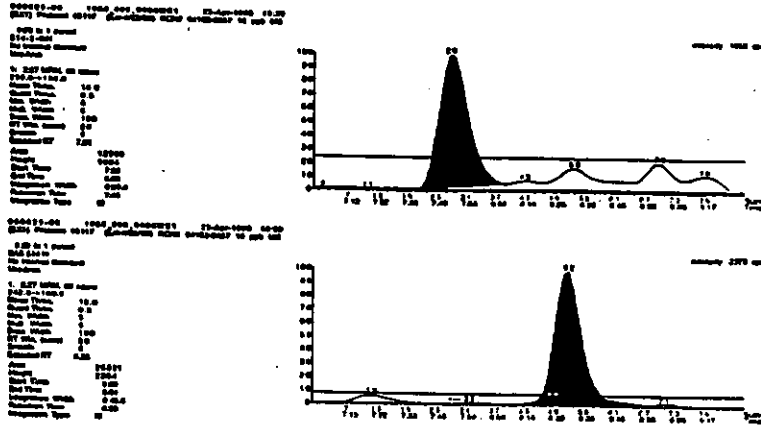
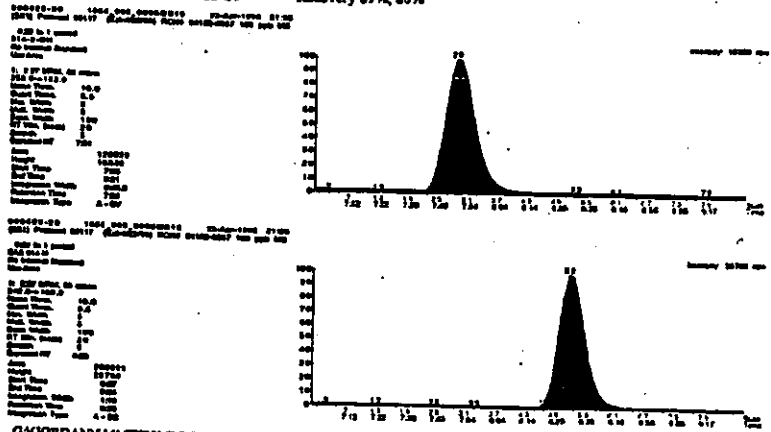


Figure J. 0.10 ppm Fortification Reflux  
BAS 514, BH 514-2-OH  
Sample 960423-20 Recovery 89%, 80%



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

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000000.00 000000.00 000000.00
-----
0.10 ppm Fortification
Sample 030196-11
Recovery 92%

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