BASF CORPORATION CHEMICALS DIVISION
Agricultural Chemicals
100 Cherry Hill Road
Parsippany, New Jersey 07054

410635-37

Study Title

GLC method for residue determinations of Quinclorac (3,7-Dichloro - 8 -quinolinecarboxylic acid) in rice grain, straw, hulls, bran and polished grain.

Data Requirements

EPA Guideline Number: 171-4

Author

Dr. David McAleese

Study Completed On

March, 1989

Performing Laboratory

BASF Corporation
Agricultural Chemicals Division
26 Davis Drive
Research Triangle Park, NC 27709

Registration Document No. BASF:

89/5004

This report consists of 28 pages.

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 Chemicals Group

Company Agent: D.W. Huntington, for 3/22/89
Jack R. Graham Date
Manager, Registration

GOOD LABORATORY PRACTICES STATEMENT

This study meets the requirements for 40 CFR 160, Good Laboratory Practices.

Company: BASF CORPORATION
Agricultural Chemicals Group

Submitter and Sponsor: _____ 3/22/89
Jack R. Graham
Manager, Registration
Date

Study Director: SEE PAGE 89-5004 0005

GLC Method for Residue Determinations of Quinclorac

(3,7-Dichloro-8-quinolinecarboxylic acid)

in Rice Grain, Straw, Hulls, Bran and Polished Grain

Method No. A8902

Date Issued: March, 1989

Study Performed by: BASF Corporation
Agricultural Chemicals Division
26 Davis Drive
Research Triangle Park, NC 27709

Study Director: Dr. David McAleese
Senior Agricultural Research Chemist
Residue Analytical Group
Tel. (919) 248-6648

Method No. A8902

QUALITY ASSURANCE STATEMENT

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

Analysts: Alan Shore Date: March 16, 1989
Alan Shore
Agricultural Technician

Study Director: David McAleese Date: March 16, 1989
Dr. David McAleese
Senior Agricultural Research Chemist

Approved By: Robert C. Paulick Date: March 16, 1989
Dr. Robert C. Paulick
Group Leader, Residue Analysis

Issued By: Nancy Cargile Date: 3/16/89
Dr. Nancy L. Cargile
Manager, Chemistry Section

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1 INTRODUCTION AND SUMMARY

1.1 Scope and Source of the Method

1.1.1 Scope

Metabolism investigations showed that quinclorac residues in rice matrices consist of the parent compound only. Therefore this method was based on the determination of the active ingredient by GC with electron capture detection, after methylation.

1.1.2 Source

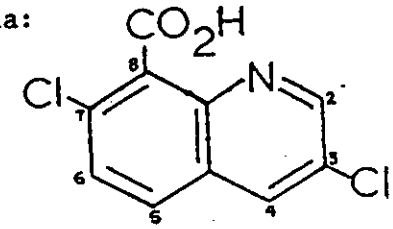
This method is a revision of Method 266 (Ref. 1), developed by Dr. Frank Mayer in BASF's laboratories in Limburgerhof, Germany, with subsequent revisions in the BASF laboratories in North Carolina to make it compatible with materials and crops available in the US, and to change the order of derivatization and column clean-up steps.

This method has also been used for analyzing several rotational crop matrices. Modifications are included in the analytical procedure as needed.

1.2 Substance

Common name: Quinclorac
Laboratory number: 150 732
BAS-number: BAS 514 H
Chemical name: 3,7-Dichloro-8-quinolinecarboxylic acid

Structural formula:



Empirical formula: $C_{10}H_5Cl_2NO_2$
Molecular weight: 242.1
Melting point: Above 237° C decomposition
Appearance: Crystalline, colourless
Odour: Weak

Solubility: (g substance in 100 g solvent at 20° C)

Water	6.2×10^{-3}
Ethanol	0.2
Acetonitrile	<0.1
Acetone	0.2
Ethylacetate	0.1
Dichloromethane	<0.1
Diethylether	0.1
Toluene	<0.1
n-Hexane	<0.1
Olive oil	<0.1

1.3 **Principle of Method**

The sample is swollen in 0.1 N NaOH and extracted with acetone. Interferences are removed by dichloromethane partition at pH = 8. The sample is acidified and the active ingredient is partitioned into dichloromethane. After methylation, quinclorac residues are separated on a silica gel column and determined by capillary gas liquid chromatography with electron capture detection (ECD).

Limits of determination and sensitivity: 0.05 mg/kg.

2 MATERIALS AND METHODS

2.1 **Equipment**

Bottles, amber, screw cap	4 oz.
Buchner funnel	10 cm, 12 cm i.d.
Centrifuge tube	15.0 mL (calibrated), 50.0 mL
Filter flask	1 Liter
Flat bottom flask with standard ground joint	500 mL, 1 Liter
Funnels	4 cm, 10 cm i.d.
Graduated cylinder	250 mL
Volumetric flasks	25.0 mL, 50.0 mL, 100.0 mL, 200.0 mL, 500.0 mL
Volumetric pipettes	0.5 mL, 1.0 mL, 2.0 mL, 5.0 mL 10.0 mL, 20.0 mL, 100.0 mL
Blender, high speed	Waring
Blender jar, 1 quart	Waring, Fisher Scientific
Capillary Gas Chromatograph with ^{63}Ni ECD	Eg. Varian 6000 or 3700
Capillary GC column DB5 (megabore)	J&W Scientific Rancho Cordova, CA
N-evap (Nitrogen Stream Evaporator)	Organomation Assoc. Northborough, MA
Rotary Evaporator	Buchi or equivalent
Supelco Vacuum Manifold	Supelco, Bellefonte PA
Ultrasonic Bath	Branson 1200 or equivalent

Filter aid e.g., Celite type 545	Fisher Scientific Delmar Newark, DE #C212-500
Filter paper (Whatman No. 4) 9 cm, 11 cm i.d.	Whatman Limited, England Fisher Scientific, Delmar, Newark, DE #1004090
Phase Separating filter	Fisher Scientific, Delmar, Newark, DE #2200110
Prepacked silica gel solid phase extraction column; 3mL	J.T. Baker Phillipsburg, NJ
Universal pH indicator sticks or paper, pH 0-14, pH 0-2.5	EM Science Cherry Hill, NJ #9580, 9590

2.2 **Reagents and Chemicals**

Acetic acid, glacial, reagent ACS	J.T. Baker Phillipsburg, NJ CAS 64-19-7
Acetone, distilled, high purity	Burdick & Jackson
Carbitol	Aldrich, Milwaukee, WI D2,800-0
Dichloromethane, distilled, high purity	Burdick & Jackson
Diethyl ether, anhydrous reagent ACS	Fisher Scientific Fairlawn, NJ CAS 60-29-7
Hexane, distilled, high purity	Burdick & Jackson
Methanol, distilled, high purity	Burdick & Jackson
N-Methyl-N-nitroso-p-toluenesulfonamide (Diazald)	Aldrich, Milwaukee, WI D2, 800-0
Potassium Hydroxide analytical reagent- 60% in deionized water	Mallinckrodt Paris, KY #6984
Sodium Bicarbonate powder, analytical grade	Fisher Scientific Fairlawn, NJ CAS 144-55-8
Sodium hydroxide pellets, reagent ACS	Kodak, Rochester, NY Cat 137 6466
Sodium hydroxide solution 0.1N(0.1 mol/L) in water	
Sulfuric acid, concentrated analytical grade	J.T. Baker Phillipsburg, NJ CAS 7664-93-9
Water, deionized	

2.2.1 SPE Eluting Solvent

Prepare a 75% DCM:hexane solution as follows:

Place 75 mL of dichloromethane in a graduated cylinder or volumetric flask. Bring to 100 mL with hexane.

2.2.2 Preparation of Diazomethane Solution

Preparation of diazomethane solution (in a hood): Assemble two test tubes, each fitted with a 2-holed rubber stopper and connected in series with plastic tubing. Add a few milliliters of diethyl ether to test tube A. Add about 50 mL of diethyl ether to a 50 mL screw cap volumetric flask. Add 2.0 mL of carbitol, 2.0 mL of 60% potassium hydroxide in deionized water, 2.0 g of Diazald, and 2.0 mL of diethyl ether to test tube B. Use the ether solution to rinse the walls of the test tube. Slowly bubble nitrogen into the solution in test tube A, from test tube A into the solution in test tube B, and from test tube B into the solution in the volumetric flask. Allow gas to escape from the volumetric flask into the hood. Continue bubbling nitrogen until the yellow color in test tube B dissipates and a deep yellow color persists in the volumetric flask with no further intensification of the color. The level of diazomethane in the volumetric flask is adequate for a set of 8 samples. Quench any remaining diazomethane solution in test tube B with acetic acid. The yellow color will disappear.

2.3 Standard Substances and Solutions

Quinclorac (structure page 5)	>99.5%
3,7-Dichloro-8-quinolinecarboxylic acid methylester	>99.5%

Store standards in a freezer.

(both standards supplied by: Dr. Ohnsorge, BASF
Aktiengesellschaft, APE/CU
Agricultural Research Center
D-6703 Limburgerhof
Tel. 06236/68-417)

2.3.1 Standard solutions for fortifications:

Quinclorac 1000; 10.0; 1.0; and 0.1 µg/mL in methanol

Store the standard BAS 514 solid in a freezer when not in use. Store standard solutions of BAS 514 H in an amber bottle with a plastic lined screw cap and refrigerate. Prepare a 1.00 mg/mL BAS 514 H stock solution by weighing 25.0 mg of BAS 514 H into a 25 mL volumetric flask. Dissolve with methanol and dilute to the mark.

Prepare a 10.0 µg/mL BAS 514 H standard solution by transferring 1 mL of the 1.00 mg/mL stock solution with a volumetric pipet to a 100 mL volumetric flask. Dilute to the mark with methanol. Prepare a 1.00 µg/mL BAS 514 H standard solution by transferring 10 mL of the 10.0 µg/mL BAS 514 H solution with a volumetric pipet to a 100 mL volumetric flask. Dilute to the mark with methanol.

Prepare a 0.100 µg/mL BAS 514 H standard solution by transferring 10 mL of the 1.0 µg/mL standard solution with a volumetric pipet to a 100 mL volumetric flask. Dilute to the mark with methanol.

2.3.2 Standard solutions for GLC analysis:

3,7-Dichloro-8-quinolinecarboxylic acid methylester
10, 20, 40, 80, 400 ng/mL; 20 µg/mL and 1 mg/mL in acetone

Prepare a 1.00 mg/mL BAS 514 methyl ester stock solution by weighing 25.0 mg of BAS 514 methyl ester into a 25 mL volumetric flask. Dissolve with acetone and dilute to the mark.

Prepare a 20.0 µg/mL BAS 514 methyl ester solution by transferring 2 mL of the 1.00 mg/mL stock solution with a volumetric pipet to a 100 mL volumetric flask. Dilute to the mark with acetone.

Prepare a 400 pg/µL BAS 514 methyl ester solution by transferring 2 mL of the 20.0 µg/mL solution with a volumetric pipet to a 100 mL volumetric flask. Dilute to the mark with acetone.

Prepare an 80.0 pg/µL BAS 514 methyl ester standard solution by transferring 20 mL of the 400 pg/µL solution with a volumetric pipet to a 100 mL volumetric flask. Dilute to the mark with acetone.

Prepare a 40.0 pg/µL BAS 514 methyl ester standard solution by transferring 10 mL of the 400 pg/µL solution with a volumetric pipet to a 100 mL volumetric flask. Dilute to the mark with acetone.

Prepare a 20.0 pg/µL BAS 514 methyl ester standard solution by transferring 5 mL of the 400 pg/µL solution with a volumetric pipet to a 100 mL volumetric flask. Dilute to the mark with acetone.

Prepare a 10.0 pg/µL BAS 514 methyl ester standard solution by transferring 5 mL of the 400 pg/µL solution with a volumetric pipet to a 200 mL volumetric flask. Dilute to the mark with acetone.

Transfer these standard BAS 514 methyl ester solutions to an amber bottle with a plastic lined screw cap and store the solutions in a refrigerator when not in use.

2.3.3 Stability of standard solutions (Ref. 1):

Storage Days	Room temperature Daylight	4°C Refrigerator
	3,7-Dichloro-8-quinolinecarboxylic acid methylester 0.2 µg/mL in acetone	
7	99.7%	103.8%
35	100.1%	100.8%
106	-	101.1%

3 ANALYTICAL PROCEDURE

3.1 Extract Preparation

3.1.1 Preparation of Samples

All samples are finely ground. The samples are then stored at -20°C until analysis.

3.1.2 Extraction and Fortification

Weigh 10.0 g of crop into a one-quart blender jar.

At least two fortifications and ~~one untreated sample~~ (= control) are run with each set of samples. The amount of quinclorac for fortification trials should be on the order of the expected residue.

For the 0.05 ppm fortification samples, pipet 5 mL of a 0.100 µg/mL standard BAS 514 H solution with a volumetric pipet onto the crop. For the 1.0 ppm fortification samples, pipet 1 mL of a 10.0 µg/mL standard BAS 514 H solution with a volumetric pipet onto the crop.

Add 100 mL of aqueous 0.1 N sodium hydroxide and allow to soak for at least 1 hour. Add 200 mL of acetone. For soybean grain samples, also add about 20 g of Celite 545. Blend for 3 minutes using a high-speed blender.

Add approximately 20 g of Celite 545 on top of two Whatman No. 4 filters (9 cm diameter) in a Buchner funnel. For soybean grain samples, add about 40 g of Celite 545 on top of two Whatman No. 4 filters (11 cm diameter) in a Buchner funnel. Wet the filter paper with deionized water before use. Filter the sample with aspiration and collect the filtrate in a 1 L filter flask. Keep the marc saturated with acetone during filtration. Rinse the blender jar thoroughly with acetone and filter. Rinse the marc thoroughly with acetone and filter. Discard the marc.

Quantitatively transfer the filtrate to a 1 L flat bottom flask using acetone transfer washings and acidify with 3.0 mL of concentrated sulfuric acid.

Do not store any of the solutions to this point in the procedure. With subsequent steps, solutions may be stored at room-temperature.

Concentrate the extract to approximately 75 mL using a rotary evaporator with a water bath maintained at 50°C. Do not allow the solution to evaporate to the 50 mL level, because solid residues that are difficult to solubilize may collect on the inside of the flask.

3.1.3 First Dichloromethane Partition

Carefully add sodium bicarbonate to the solution (Caution: foaming will occur). After the addition of about 6 g $NaHCO_3$, foaming stops. Check pH-value with pH stick or paper and adjust to pH=8 with additional $NaHCO_3$; usually about 12 g is required.

(Optional filtration: At this point, extracts may form a solid precipitate, which can contribute towards the formation of emulsions during the partition steps. This has occurred with soybean grain, in particular. Solid precipitates can be removed from extracts by the following procedure: Add approximately 20 g of Celite 545 on top of two Whatman No. 4 filters (9 cm diameter) in a Buchner funnel. Wet the filter paper with deionized water before use. Filter the sample with aspiration and collect the filtrate in a 500 mL filter flask. Rinse the 1 L flat bottom evaporating flask thoroughly with deionized water and filter. Rinse the solids on the filter paper thoroughly with deionized water and filter.)

Quantitatively transfer the weakly alkaline aqueous solution to a 500 mL volumetric flask using deionized water transfer washings and dilute to the mark with deionized water.

Transfer 100 mL of sample extract with a volumetric pipet to a 500 mL separatory funnel. Check the pH of the aqueous solution again with pH paper. The pH must be maintained at 8.0.

pH 8 Partition: Add 100 mL of dichloromethane to the separatory funnel. Shake the solution for a few seconds and vent the flask. Repeat this procedure a few times and then allow the phases to separate. Discard the dichloromethane layer. Check the pH of the aqueous solution before each successive partition. The pH must be maintained at 8.0. Add another 100 mL of dichloromethane, shake and vent the solution a few times, allow the phases to separate, and discard the dichloromethane layer. Extract the aqueous layer a third time with 100 mL of dichloromethane for green samples such as sorghum silage and alfalfa hay.

3.1.4 Second Dichloromethane Partition

Acidify the remaining water layer with concentrated sulfuric acid (Caution: Vigorous CO_2-evolution will occur) to pH 1.0-2.0 (verify the pH with pH indicator).

Extract the aqueous phase three times with 100 mL of dichloromethane. Check the pH before each successive extraction. The pH must be maintained at 1.0 - 2.0. With each addition of dichloromethane, shake and vent the solution a few times, and allow the phases to separate.

Filter the dichloromethane extracts through Whatman phase separation filter paper into a 500 mL flat bottom flask. Rinse the material on the filter paper thoroughly with dichloromethane and filter. Discard the aqueous layer left in the separatory funnel.

Concentrate the solution to a few milliliters using a rotary evaporator with a water bath maintained at 40°C.

Quantitatively transfer the sample to a calibrated 15 mL screw cap centrifuge tube with dichloromethane transfer washings. (The centrifuge tube must be calibrated for subsequent 2.0 mL sample dilutions.) It will be necessary to use greater than 15 mL of dichloromethane in transfer washings. In order to accommodate extra transfer washings, partially evaporate the dichloromethane solution in the centrifuge tube with an N-evaporator at room-temperature.

Evaporate the solution to dryness with nitrogen on an N-evaporator at room-temperature.

3.1.5 Methylation

(All operations with diazomethane under the hood!)

Add 0.5 mL of ether and 2.0 mL of methanol to the sample and sonicate.

Pipet a few milliliters of ethereal diazomethane (see preparation of diazomethane in 2.2.2) into the sample tube. Add the same quantity of diazomethane to each sample. Seal the sample and allow to stand for about 1 hour. Add more ethereal diazomethane to the sample if the yellow color disappears in less than 30 minutes.

Evaporate the solution to dryness with nitrogen on an N-evaporator at room-temperature. Do not use a water bath and do not expose the sample to heat. Remove the sample from the N-evaporator immediately after evaporation. An oily, colored residue may remain.

Dilute to 2.0 mL with 75% DCM:hexane and sonicate.

3.1.6 SPE Column Clean-up

Attach a 3 mL Baker solid phase extraction (SPE) silica gel column to a Supelco vacuum manifold or equivalent. Open the stopcock, condition the column with 12.0 mL of the eluent, 75% dichloromethane:hexane, and allow the column to dry. Apply an additional 3.0 mL of dichloromethane:hexane eluent to the column. Allow the eluent meniscus to drop to the top bed support. Close the stopcock and discard the effluent.

Pipet 1.0 mL of sample solution with a volumetric pipet onto the silica gel column. Use a 35 mL centrifuge tube to collect the eluate. Open the stopcock, allow the sample solution meniscus to drop close to the bed support, and rinse the walls of the column above the bed support with about 0.5 mL of eluent. Allow the eluent meniscus to drop close to the bed support, and add another 0.5 mL of eluent. Allow the eluent meniscus to drop close to the bed support and fill the column with eluent. Elute the sample with an additional 24.0 mL of dichloromethane:hexane solution. Do not allow the column to dry during this process.

Evaporate the sample to dryness with nitrogen on an N-evaporator at room-temperature. Do not use a water bath and do not expose the sample to heat. Remove the sample from the N-evaporator immediately after evaporation.

3.1.7 Preparation of Final Solution

Pipette 2.0 mL of acetone or acetone-hexane mixture with a volumetric pipet into each control sample, treated sample, and 0.05 ppm fortification sample and sonicate. Treated samples may have to be diluted further. Pipet 20 mL of an acetone or acetone-hexane mixture with a volumetric pipet into each 1.0 ppm fortification sample and sonicate. Transfer the sample solution to an autosampler vial immediately.

3.2 Instrumentation

3.2.1 Description

Location of Use	BASF/Germany		BASF/US
Gas Chromatograph	Varian 3700 w/ ^{63}Ni-ECD		Varian 6000 w/ ^{63}Ni-ECD
Capillary Column	WCOT glass	WCOT fused silica	WCOT fused silica
Length	25 m	25 m	30 m
Internal Diameter	0.28 mm	0.28 mm	0.53 mm (megabore)
Stationary Phase	SE 54	OV 1701-CB	DB-5
Film Thickness	0.5 µm	0.22 µm	1.5 µm

3.2.2 Operating Conditions

Location of Use	BASF/Germany		BASF/US
Injection Temperature	270°C	270°C	230°C
Oven Temperature[1]	250°C	230 or 250°C	205°C
Retention Time	6.3 min.	6.8 or 5.0 min (depending on oven temperature)	8 min.
Run Time	-	-	12 min.
Detector Temperature	300°C	300°C	300°C
Carrier Gas	He; 700 mbar	He; 700 mbar	N_2; 9.0 mL/min.
Septum Purge	5.0 mL/min.	5.0 mL/min.	-
Split Valve	10 mL/min.	10 mL/min.	-
Make-up Gas	N_2, 30mL/min	N_2, 30 mL/min	N_2, 20 mL/min.
Injection Volume	1 µL	1 µL	1 µL
Recorder Chart Speed	0.5 cm/min.	0.5 cm/min.	-
Detector Settings	-	-	Range -10, Attenuation -16

[1]Oven temperature may be varied, depending on required peak resolution. Increasing the temperature toward the end of each run may be necessary to remove late-eluting materials which would interfere with subsequent injections. BASF/Germany used a program starting after quinclorac elution, of 230°-270° at 20°/minute and holding for 5 minutes at 270°. Hazleton Laboratories, using a DB-5 column also, used a program of 200°-240° at 10°/minute and holding for 3 minutes at 240°.

3.2.3 Calibration Procedures

Calculation of results is based on peak height measurements using a calibration curve. To obtain this standard curve inject e.g. 10, 20, 40, 80 pg quinclorac methyl ester into the gas chromatograph. Plot peak height (mm) versus amount (pg) of injected standard.

3.2.4 Sample Analysis

Inject 1 µL of each sample and each BAS 514 methyl ester standard into the gas chromatograph for analysis. Use a larger injection volume if there are sensitivity problems; however, inject the same volume for all standards and samples. For each set of samples, inject each standard at least in triplicate and inject each sample at least once. It is recommended that each sample injection be followed by an injection of acetone. Bracket the sample injections with standard injections. Inject standards every 2 - 3 samples.

3.3 **Interferences**

3.3.1 Sample Matrices

If interfering peaks occur in the chromatogram, change GC conditions (see 3.2.2).

3.3.2 Other Sources

Other Pesticides: None known to date.

Solvents: None known to date.

Labware: None known to date.

3.4 **Confirmatory Techniques**

If ECD determination fails because of interferences or peak identity is doubtful, determination can be made by GC/MS using multiple ion detection (MID) on the ions m = 224, 226, 255 and 257. Choose one or more of these ions that is/are free from interferences.

3.5 **Time Required for Analysis**

The time required for a set of 6 samples, 2 recoveries and 1 blank (= control) is 16 hours. This includes the analytical procedure, GC-injection, evaluation and report, provided that no special problems arise, such as matrix interferences.

3.6 **Potential Problems**

Not encountered up to date.

4 METHODS OF CALCULATION

4.1 **Calibration**

Measure the peak heights of the standards. Construct a polynomial least squares working curve in the form $y=ax^2 + bx + c$ or a linear least squares working curve in the form $y=ax + b$ from the standards by plotting peak height versus picograms of standard injected.

4.2 **Analyte in Sample**

Calculation of results is based on peak height measurements. Measure the peak height of the BAS 514 methyl ester peak in the samples. From the least squares working curve, determine the picograms of BAS 514 methyl ester in the samples.

Do not correct sample residues for either control residues or procedural recovery.

The residues in mg/kg (ppm) of quinclorac are calculated as follows:

$$ppm = \frac{V_E \cdot W_A \cdot D}{G \cdot V_I \cdot A}$$

G = Weight in (g) of sample extracted
V_E = Final volume after all dilution steps (ml)
V_I = µl injected from V_E
W_A = Amount of quinclorac methyl ester read from calibration curve in ng
A = Aliquot in % as a decimal, taken during sample extract processing
D = Derivatization factor = 0.945 :

$$D = \frac{\text{Molecular weight quinclorac}}{\text{Molecular weight derivative}} = \frac{242}{256} = 0.945$$

4.3 **Calculation of Recoveries**

Determine recovery factor (= F) from the fortification experiments.

$$\% \text{ Recovery} = \frac{(\text{ppm in fortified control} - \text{ppm in control}) \cdot 100}{\text{ppm quinclorac added}}$$

5 RESULTS AND DISCUSSION

5.1 Accuracy and Precision

Recovery experiments in rice matrices:

Raw Agricultural Commodity	Fortification mg/kg	Recovery %	Mean value % **	Standard Deviation ±	Variation Coefficient ±%
Rough Rice[2]	0.05* 0.50	92; 93 80	88	7.2	8.2
Rice Hulls[2]	0.05 0.50 1.0	74; 78 71 79	76	3.7	4.9
Brown Rice[2]	0.05 0.50 1.0	96; 104 85 87	93	8.8	9.4
Rice Bran[2]	0.05 0.50 1.0 2.0	72; 74; 74; 74 77; 88 64 82	76	7.1	9.4
Milled Rice[2]	0.05 0.50 1.0	72; 102 89 90	88	12	14
Average of all grain products (n=23)			82	11	13
Rice Straw[3]	0.05 1.0 5.0	74; 67; 88 88 79; 64	77	10	13
Average of all rice matrices (n=29)			81	11	13

* Determination limit

** Mean values calculated from recoveries as listed in recovery column.

5.2 Determination Limit

The determination limit for quinclorac residues in rice matrices is 0.05 mg/kg. This is the lowest amount which is proven by recovery data.

5.3 **Ruggedness Testing**

This method has been satisfactorily used in BASF's laboratories, as well as in Hazleton Laboratories America, Inc., Madison, WI, a private laboratory.

5.4 **Limitations**

None known to date.

6 CONCLUSIONS

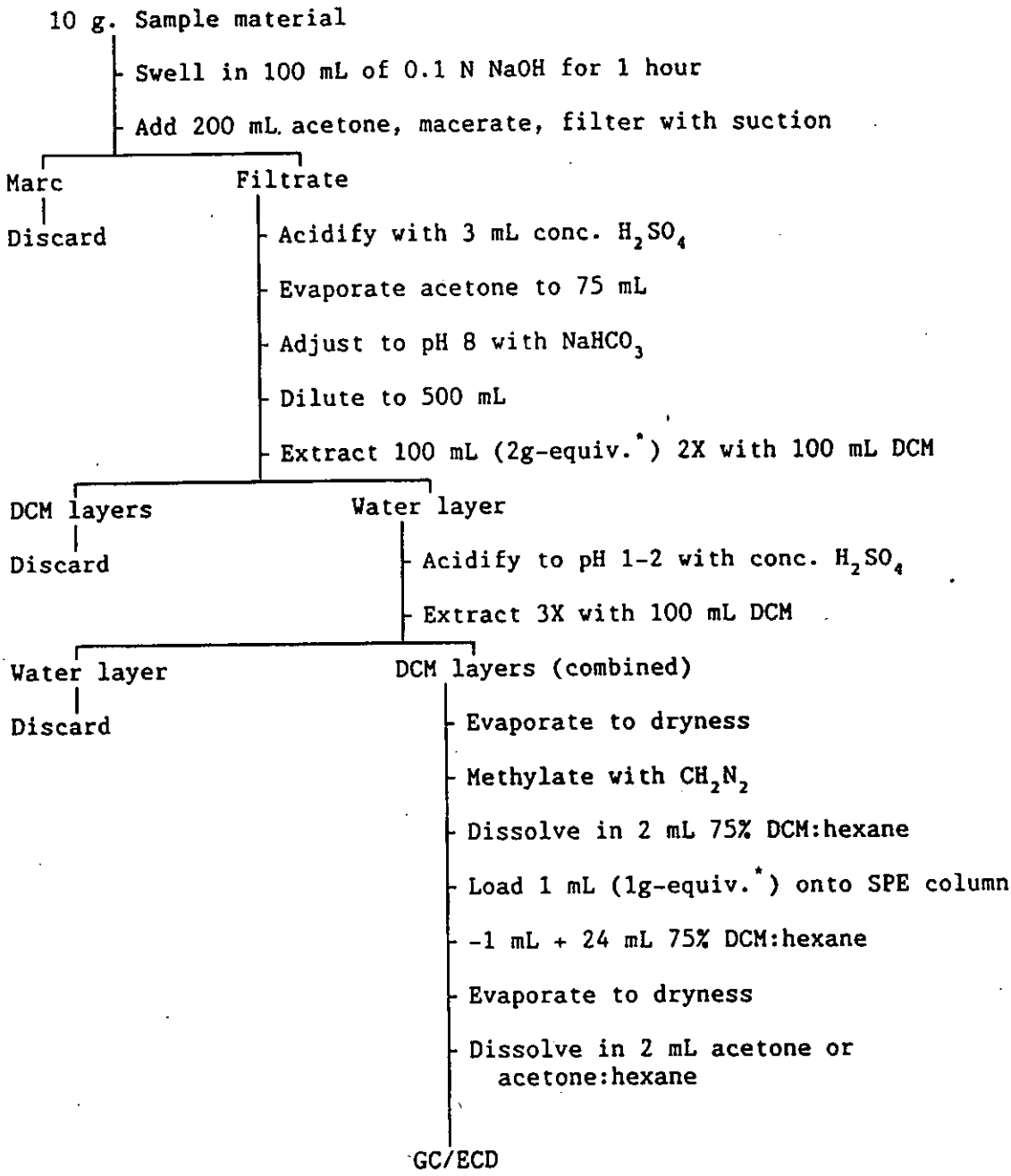
The analytical procedure is applicable for measuring residues of quinclorac in rice grain, processed products, and straw.

7 QUALITY ASSURANCE PROCEDURES

Location of raw data:

Raw data is stored in the BASF archives.

8 FLOW CHART OF ANALYTICAL PROCEDURE



* Volume equivalent to grams of sample extracted.

9 REFERENCES

1. BASF Residue Method No. 266, "GLC Method for Determinations of Quinclorac = 3,7-Dichloro-8-quinoline carboxylic Acid in Rice: Grrain, Straw, Roots, Forage", Dr. F. Mayer, February, 1987.

2. BASF Report A8905, "Magnitude of the Residue of Quinclorac in Rice Process Fractions", Y. Single, March, 1989.

3. Method Validation data, BASF Master Sheet CGR24; BASF Report A8919, Magnitude of the Residue of Quinclorac (BAS 514 H) in Rotation Crops Following Rice Culture in Louisiana (RCN 87096), March 1989.

10 FIGURES

1. Typical calibration chromatograms
2. Typical calibration curve
3. Typical rough rice chromatograms
4. Typical rice processing fraction chromatograms
5. Typical straw chromatograms

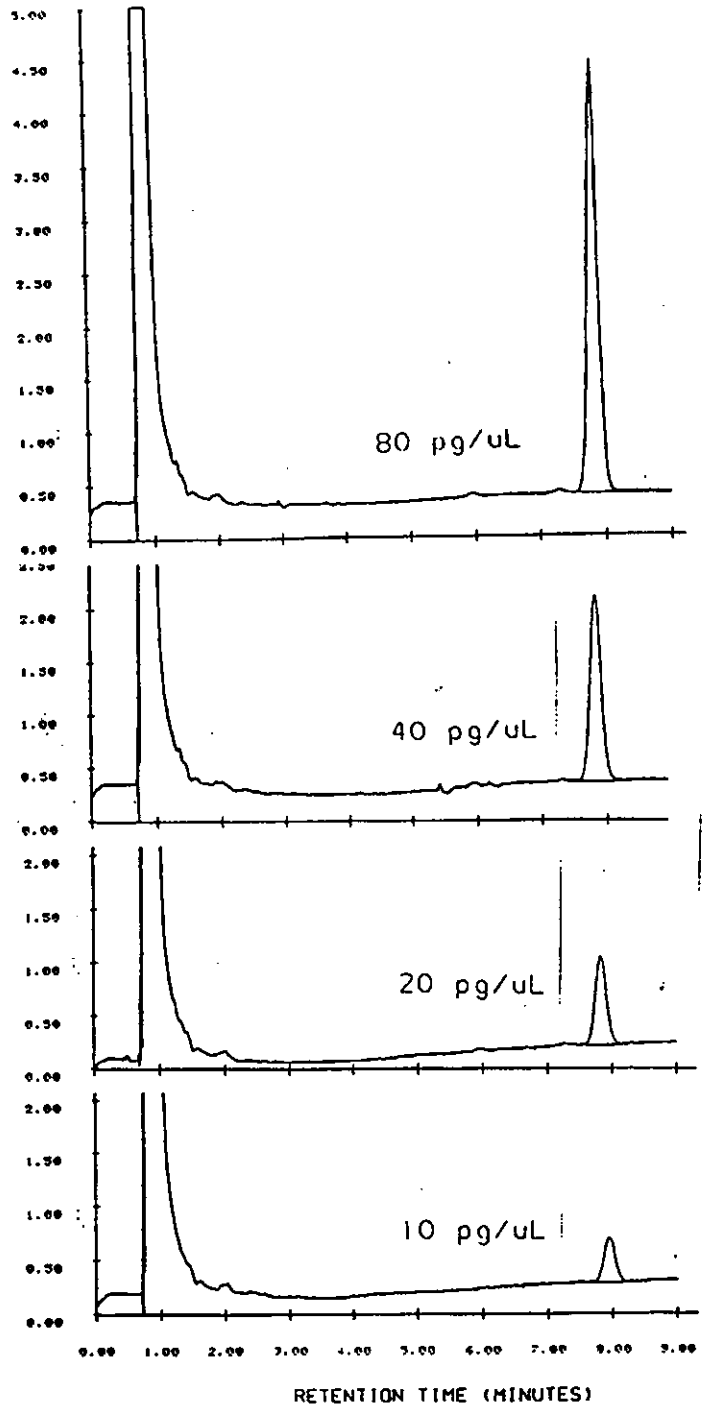


FIGURE 1. Typical Calibration Standard Chromatograms

Best fit is to a POLYNOMIAL Model of the form:
Height = a(0) + a(1)*[amt. std.] + a(2)*[(amt. std.)^2] + ...
a(0) is 145.166667
a(1) is 132.398871
a(2) is .674059139

For X	Yinput	Ycalc	Diff
10.000	1545.000	1536.561	8.439
20.000	3048.000	3062.768	-14.768
40.000	6527.000	6519.616	7.384
80.000	15050.000	15051.055	-1.055

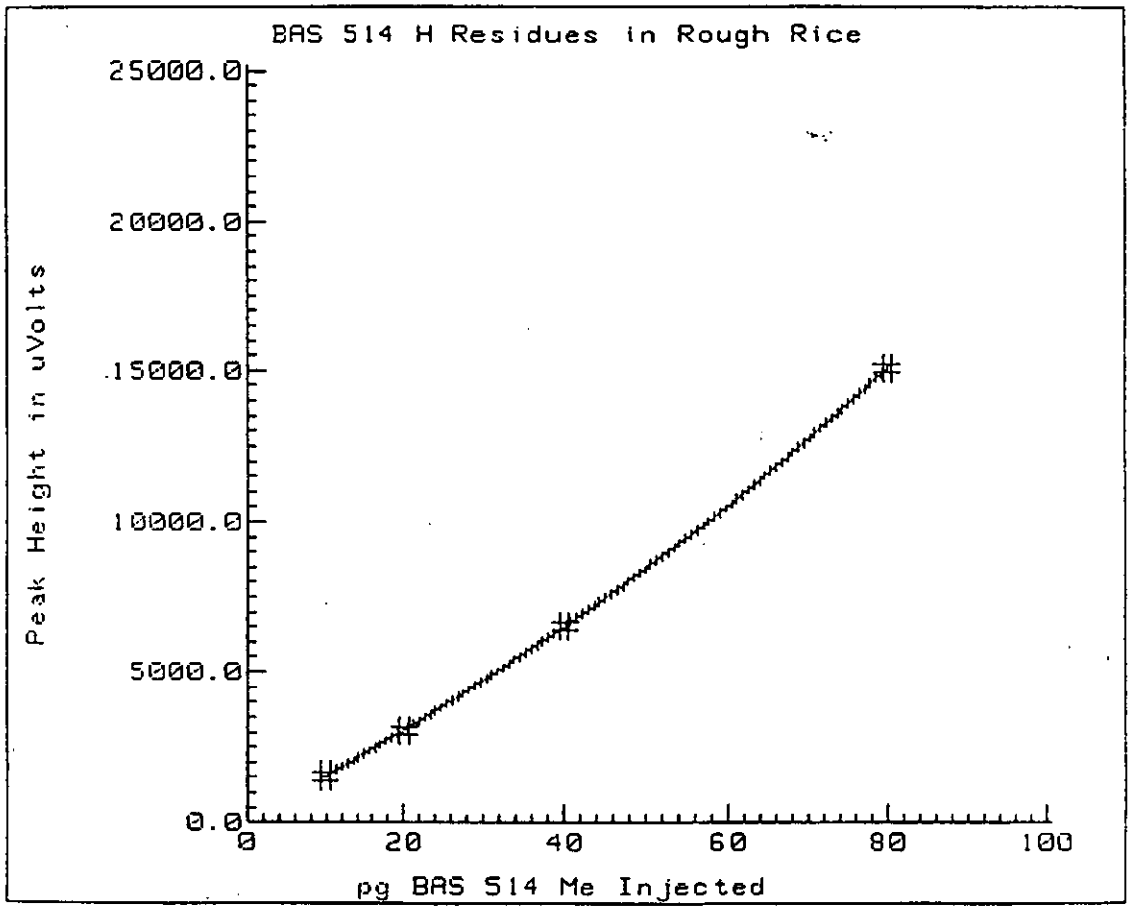


FIGURE 2. Typical Calibration Curve

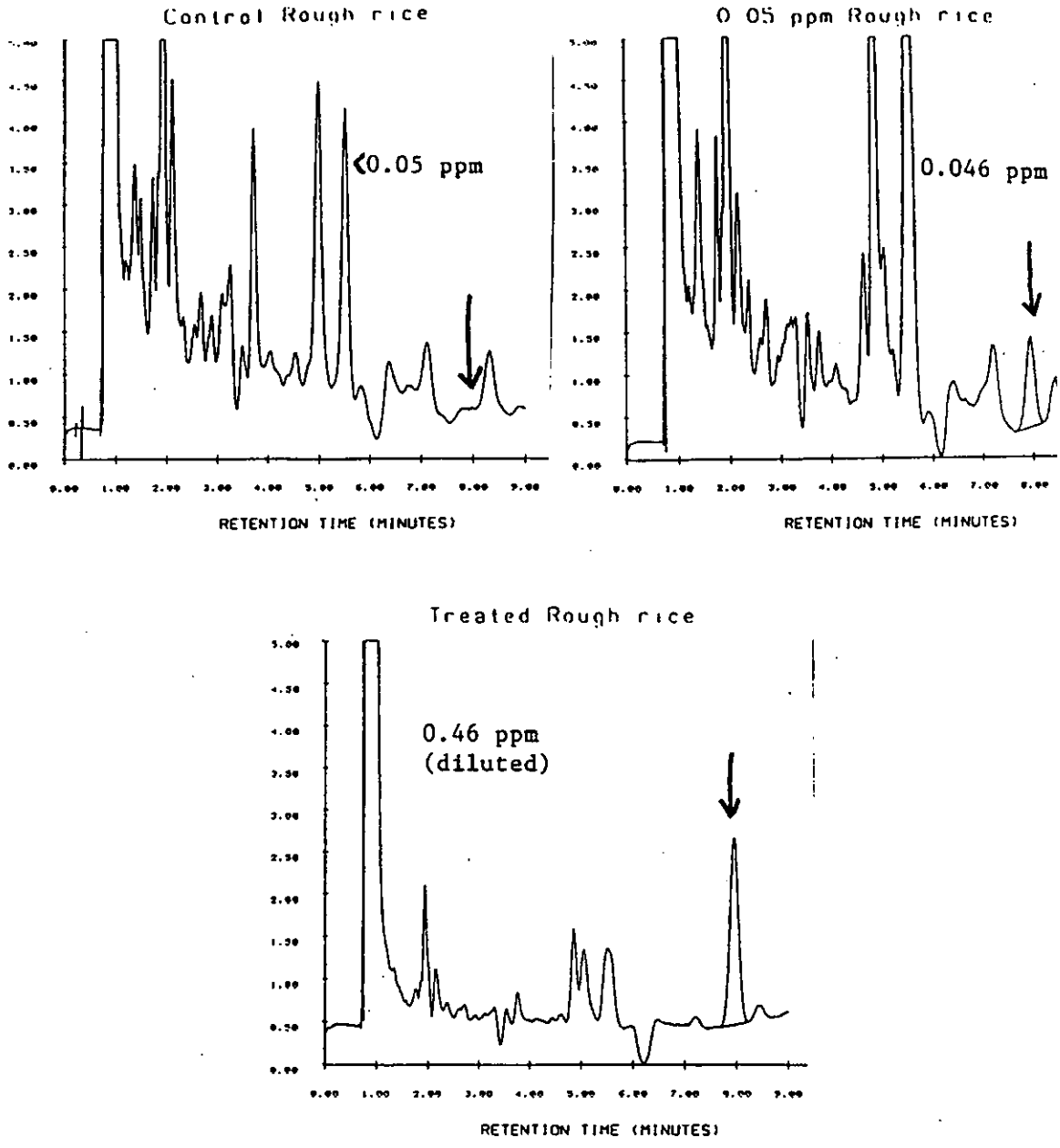


FIGURE 3. Typical Rough Rice Chromatograms -
Control, Fortified (0.05 ppm) and Treated Samples

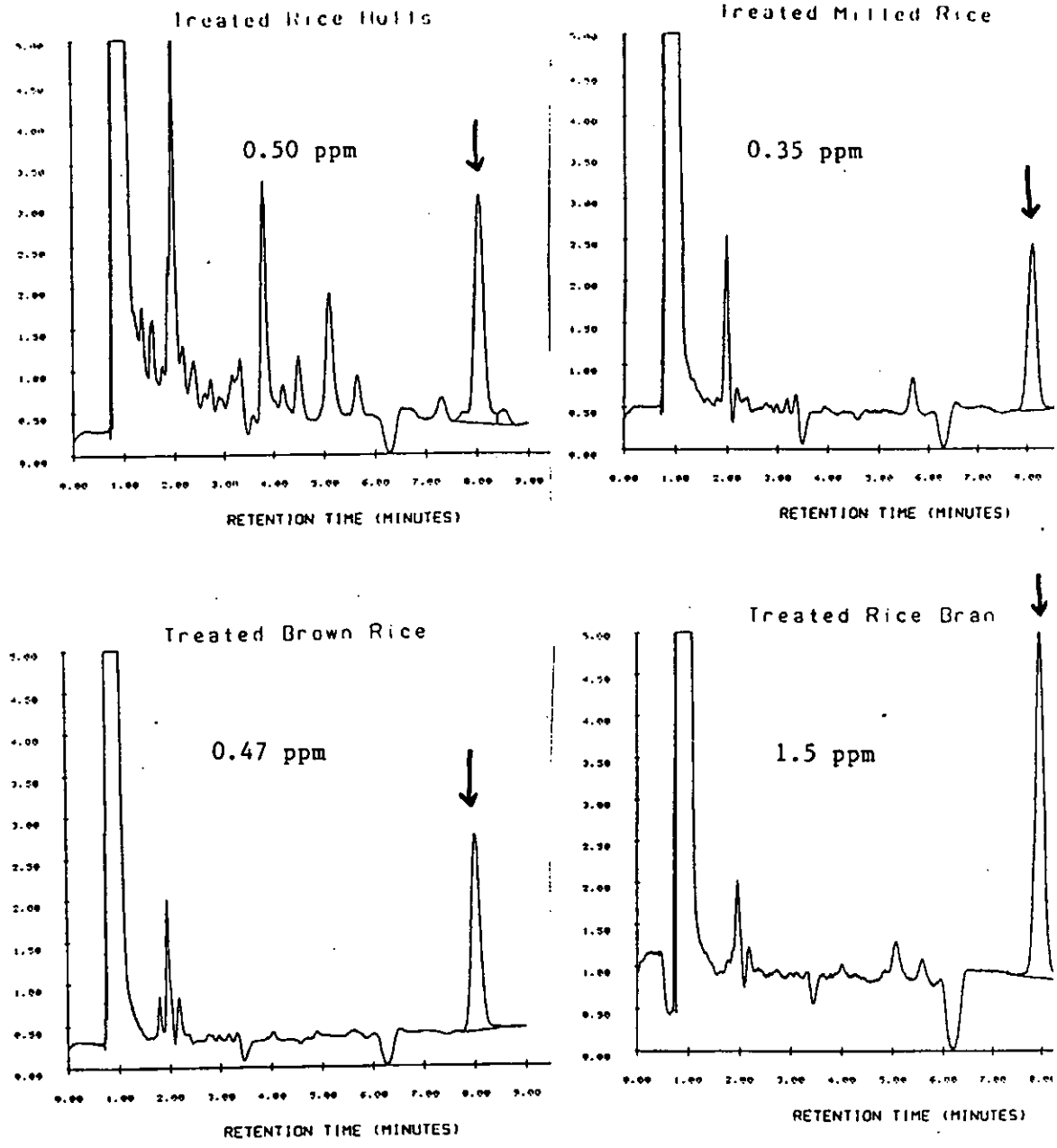
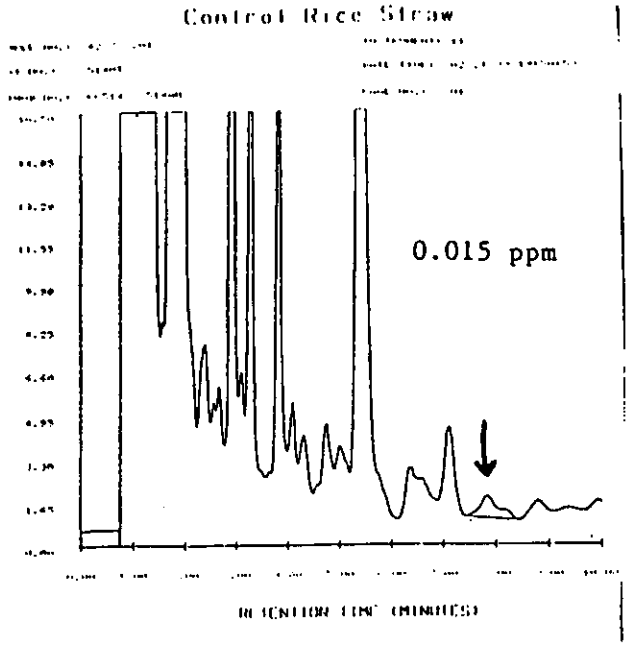
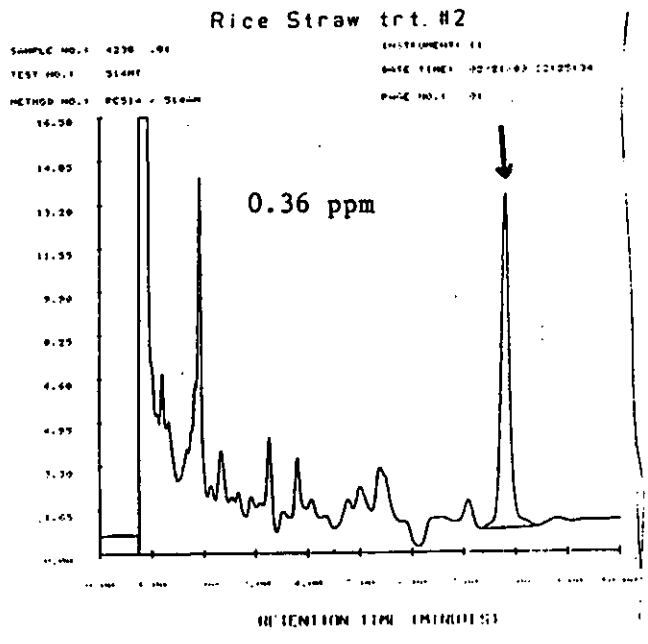


FIGURE 4. Typical Processing Fraction Chromatograms - Hulls, Bran, Brown Rice, Milled Rice





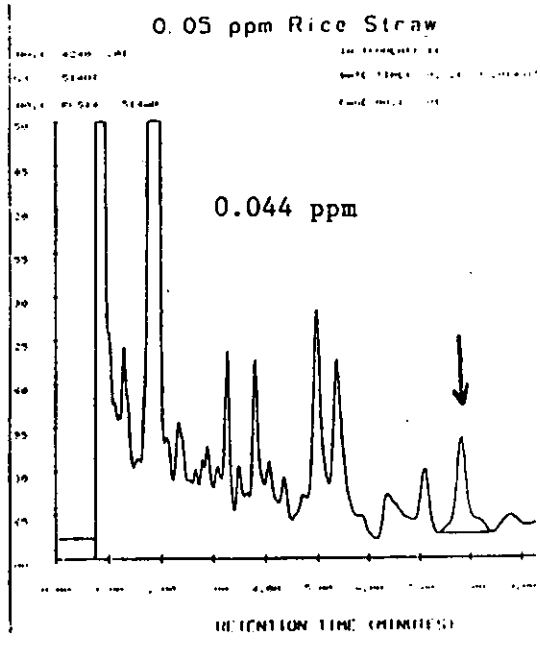


FIGURE 5. Typical Straw Chromatograms