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**Method for Determination of Residues  
of Pyridaben in Oranges and Orange Processed Commodities  
by Gas Chromatography**

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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

Company Agent: Rodney Akers

Date: May 10, 1994

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GOOD LABORATORY PRACTICE COMPLIANCE STATEMENT

This study meets the requirements for 40 CFR Part 160.

Submitter: Rodney C. Aiken May 10, 1994

Sponsor: Rodney C. Aiken May 10, 1994

Study Director: Jeffrey D. Burkey  
Jeffrey D. Burkey

## QAU STATEMENT

Method Number: D9309  
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Study Initiation Date: July 14, 1993

The quality assurance unit of the testing facility at the ARC has audited the protocol, the analytical portion including the raw data, and the report for this study and reported its findings to the study director and to management.

<u>Date of Audit</u>	<u>Report to Study Director and to Management</u>
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\_\_\_\_\_  
Signature of QAU

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**Method for Determination of Residues  
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by Gas Chromatography**

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Method No. D9309

Report Date: April 7, 1994

**ABSTRACT:**

Analytical Method Number D9309 was developed to determine the residues of Pyridaben (BAS 300 I) in oranges and orange processed commodities. Method development and validation were carried out at BASF Corporation, Research Triangle Park, N.C., using representative control orange and orange processed commodities. Pyridaben is extracted from all matrices except oil by using an acetone/water solution. For oil, the compound is extracted by dissolving the matrix in hexane and then partitioning with acetonitrile. For all matrices except oil, extracts are purified by a series of partitions. Pyridaben is partitioned from the extract into hexane, and then from hexane the compound is partitioned into acetonitrile. For molasses only, the acetonitrile volume is reduced, dichloromethane is added, and the solution is washed with water. All matrices are further purified with either florisil (whole orange, juice, oil) or silica gel (molasses, dried pulp, peel). In addition, oil, dried pulp, and peel samples are additionally purified using C<sub>18</sub> solid phase extraction. A gas chromatography system with electron capture detection is used for the final determination.

This method also includes an alternative procedure for whole oranges in which the pyridaben is partitioned from the extract with dichloromethane and then purified with a "mini" hand packed silica gel column prior to final analysis.

**ABSTRACT CONTINUED:**

The limit of quantitation of the method is 0.05 ppm for each matrix. The average recoveries from the validation data over a range of 0.05 to 5.0 ppm fortifications was 87±7% (N=18) for whole oranges, 85±5% (N=27) for whole oranges analyzed by the alternative procedure, 92±9% (N=18) for orange peel, 95±4% (N=18) for orange juice, 86±7% (N=18) for dried orange pulp, 81±15% (N=27) for orange molasses, and 83±7% (N=18) for orange oil.

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## TABLE OF CONTENTS

	Page
DATA CONFIDENTIALTY STATEMENT . . . . .	2
GOOD LABORATORY PRACTICE COMPLIANCE STATEMENT . . . . .	3
STATEMENT OF THE QUALITY ASSURANCE UNIT . . . . .	4
ABSTRACT . . . . .	5
TABLE OF CONTENTS . . . . .	7
1 INTRODUCTION AND SUMMARY . . . . .	10
1.1 Scope and Source of the Method . . . . .	10
1.1.1 Scope . . . . .	10
1.1.2 Source . . . . .	10
1.2 Substance . . . . .	10
1.3 Principle of the Method. . . . .	11
2 MATERIALS . . . . .	11
2.1 Equipment . . . . .	11
2.2 Reagents and Chemicals . . . . .	12
2.3 Standard and Standard Stability. . . . .	12
2.4 Standard Solutions for Fortifications . . . . .	12
2.5 Standard Solutions for IC Analysis . . . . .	13
3 ANALYTICAL PROCEDURE . . . . .	13
3.1 Preparation of Samples . . . . .	14
3.2 Method for Whole Orange and Orange Juice . . . . .	14
3.2.1 Extraction . . . . .	14
3.2.2 Hexane Partition . . . . .	14
3.2.3 Hexane/Acetonitrile Partition . . . . .	15
3.2.4 Florisil Column Clean-Up . . . . .	15
3.3 Alternative Procedure for Whole Orange . . . . .	16
3.3.1 Extraction . . . . .	16
3.3.2 DCM Partition . . . . .	17
3.3.3 Mini-Silica Gel Column Chromatography . . . . .	17
3.4 Method for Orange Peel . . . . .	18
3.4.1 Extraction . . . . .	18
3.4.2 Hexane Partition . . . . .	18
3.4.3 Hexane/Acetonitrile Partition . . . . .	18
3.4.4 Silica Column Clean-Up . . . . .	18
3.4.5 C <sub>18</sub> Column Clean-Up . . . . .	19
3.5 Method for Dried Orange Pulp . . . . .	19
3.5.1 Extraction . . . . .	19
3.5.2 Hexane Partition . . . . .	19
3.5.3 Hexane/Acetonitrile Partition . . . . .	19
3.5.4 Silica Column Clean-Up . . . . .	20
3.5.5 C <sub>18</sub> Column Clean-Up . . . . .	20
3.6 Method for Orange Molasses . . . . .	20
3.6.1 Extraction . . . . .	20
3.6.2 Hexane Partition . . . . .	20
3.6.3 Hexane/Acetonitrile Partition . . . . .	20
3.6.4 Water/DCM Partition . . . . .	21
3.6.5 Silica Column Clean-Up . . . . .	21

## TABLE OF CONTENTS (continued)

	Page
3.7	Method for Orange Oil . . . . . 21
3.7.1	Extraction . . . . . 21
3.7.2	Florisil Column Clean-Up . . . . . 21
3.7.3	C <sub>18</sub> Column Clean-Up . . . . . 21
3.8	Instrumentation . . . . . 22
3.8.1	Description of Equipment . . . . . 22
3.8.2	Typical Operating Conditions . . . . . 22
3.8.3	Calibration Procedures . . . . . 23
3.8.4	Sample Analysis . . . . . 23
3.9	Interferences . . . . . 23
3.9.1	Sample Matrices. . . . . 23
3.9.2	Other Sources. . . . . 23
3.10	Confirmatory Techniques. . . . . 23
3.10.1	Description of Equipment . . . . . 24
3.10.2	Operating Conditions . . . . . 24
3.11	Time Required for Analysis . . . . . 24
3.12	Potential Problems and Helpful Hints . . . . . 24
4	METHODS OF CALCULATION . . . . . 25
4.1	Principle. . . . . 25
4.2	Calculation of Residues. . . . . 25
4.3	Calculation of Recoveries. . . . . 26
5	RESULTS AND DISCUSSION . . . . . 26
5.1	General. . . . . 26
5.2	Accuracy and Precision . . . . . 26
5.3	Quantitation Limit . . . . . 27
5.4	Ruggedness Testing . . . . . 27
5.5	Limitations . . . . . 27
6	CONCLUSIONS . . . . . 27
7	SAFETY AND HEALTH CONSIDERATIONS . . . . . 27
7.1	General . . . . . 27
7.2	Solvents, Reagents and Standards. . . . . 27
8	CHANGES TO THE PROTOCOL . . . . . 27
9	REFERENCES . . . . . 28
10	SIGNATURES. . . . . 29

## FIGURES

1.	Whole Orange and Orange Juice Analytical Procedure . . . . .	30
2.	Alternative Procedure for Whole Orange . . . . .	31
3.	Orange Peel Analytical Procedure . . . . .	32
4.	Dried Orange Pulp Analytical Procedure . . . . .	33
5.	Orange Molasses Analytical Procedure . . . . .	34
6.	Orange Oil Analytical Procedure . . . . .	35
7.	Typical Residue Calculation . . . . .	36
8.	Typical Recovery Calculation . . . . .	37

## TABLES

I.	Summary of Validation Data . . . . .	38
II.	Summary of Analytical Standard Solution Stability Data . . . . .	39
III.	Individual Validation Data for Whole Oranges . . . . .	40
IV.	Individual Validation for Whole Oranges (Alternative Procedure) . . . . .	41
V.	Individual Validation Data for Orange Peel . . . . .	42
VI.	Individual Validation Data for Orange Juice . . . . .	43
VII.	Individual Validation Data for Dried Orange Pulp . . . . .	44
VIII.	Individual Validation Data for Orange Molasses . . . . .	45
IX.	Individual Validation Data for Orange Oil . . . . .	46
X.	Individual Analytical Standard Solution Storage Stability Data . . . . .	47
XI.	Summary of Standard Data . . . . .	48

## APPENDICES

A.	Deviations and Amendments to the Protocol . . . . .	49
B.	Typical Raw Data and Chromatograms . . . . .	51

1. Introduction and Summary1.1 Scope and Source of the Method1.1.1 Scope

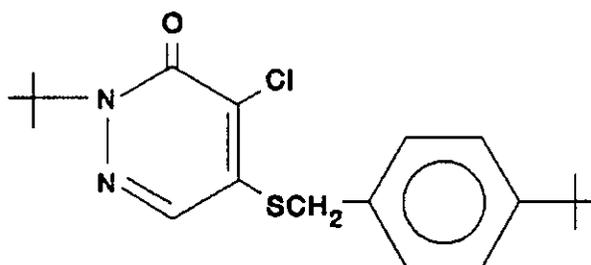
The purpose of this study was to provide validation data for the analyses of pyridaben (BAS 300 I), an acaricide developed for mite control in fruit crops, in oranges and its processed commodities (peel, juice, dried pulp, molasses and oil). Additionally, this study was designed to provide stability data for the test substance under typical analytical standard solution storage conditions. This report describes the analytical procedures validated as well as the results of the validation and stability analyses.

1.1.2 Source

This method was developed at the BASF Agricultural Research Center in Research Triangle Park, North Carolina. The method is a modification and extension of the analytical procedure developed by BASF Aktiengesellschaft Product Safety Crop Protection Group for the determination of pyridaben residues in plants (Reference 1).

1.2 Substance

Common Name: Pyridaben  
 BAS Number: BAS 300 I  
 Chemical Name: 4-chloro-2-(1,1-dimethylethyl)-5-  
 [[[4-(1,1)-dimethyl-ethyl)phenyl]  
 methyl]thio]-3(2H)-pyridazinone  
 CAS Name: 96489-71-3  
 Structural Formula:



Empirical Formula:  $C_{19}H_{25}ClN_2OS$   
 Molecular Weight: 364.9 g/mole  
 Melting point: 111-112°C  
 Boiling point: NA  
 Appearance: White Crystalline Solid

Solubility: (g/100 mL solvent at 20°C)

Acetone	46	Ethanol	5.7
Acetonitrile	6.9	n-Hexane	1.0
Dichloromethane	15.3	Water	$1.2 \times 10^{-6}$

### 1.3 Principle of the Method

Pyridaben is extracted from homogenized plant material using an acetone/water solution, except for oil, which is dissolved in hexane and partitioned into acetonitrile. The residues are purified by a series of partitions using hexane, acetonitrile, or dichloromethane, depending upon the matrix. Further purification is achieved by column chromatography (florisil, silica gel and/or C<sub>18</sub>, depending upon the matrix). The eluent from the column is analyzed by gas chromatography with electron capture detection.

## 2. MATERIALS

### 2.1 Equipment-Suggested Sizes/Manufacturer

The following laboratory equipment is recommended for use with the method and was used for the validation analyses. Equipment which is equivalent in purpose may be used.

Flat-bottom flask, 24/40	50 mL, 125 mL, 250 mL, 500 mL, 1000 mL
Glass Buchner Funnel	90 mm diameter
Filter Flask	500 mL
Wideneck Screw-cap Glass Bottle	250 mL
Separatory Funnel	125 mL, 250 mL, 500 mL
Funnel, long stem	75 mm diameter; 150 mm stem
Funnel, short stem	75 mm diameter, 75 mm stem
Volumetric Flask	25 mL, 50 mL, 100 mL, 500 mL
Volumetric Pipette	0.5-10 mL
Chromatographic Glass Column	i.d. 15 mm, 11 mm, 25 cm length
Glass SPE Column w/frit	8 mL, Burdick and Jackson
Glass Reservoir	50 mL, Burdick and Jackson
Reservoir Adaptor, Teflon	Burdick and Jackson
Centrifuge Bottles	250 mL
Filter Paper	Whatman 1PS-11 cm, No. 4-24 cm, and No.5-9 cm
Pyrex Centrifuge Tube with screw cap	15 mL, 50 mL
Autosampler Vials 1.5 mL	Sun Brokers, Inc.
Autosampler Caps 11 mm snap caps	Sun Brokers, Inc.
Glass Wool	e.g. sterile
Ultrasonic Bath	Branson 1200
Centrifuge	Beckman
Nitrogen Stream Evaporator	N-Evap Organomation Assoc., Inc.
Stirring Plate	Corning
Magnetic Stir Bar	
Balance (with at least one-tenth of a gram capability)	Mettler
Polytron Homogenizer	Brinkmann Instruments
SPE Manifold	Supelco, Inc.
Mechanical Shaker	Janke & Kunkel HS501D
Rotary Evaporator	Buchi Rotovapor
Vortex Mixer	Fisher Scientific

2.2 Reagents and Chemicals - Source/Preparation

<u>Reagents and Chemicals</u>	<u>Source/Preparation</u>
Acetone	Distilled, high purity [Burdick & Jackson (B & J)]
Deionized water	
Dichloromethane (DCM)	Distilled, high purity (B & J)
Acetonitrile (ACN)	Distilled, high purity (B & J)
Hexane	Distilled, high purity (B & J)
Ethyl Acetate	Distilled, high purity (B & J)
Toluene	Distilled, high purity (B & J)
Ethyl Ether	Krackler Scientific, Inc. (Includes 2% alcohol, from manufacturer) Cat.# 0853-040
Hydrochloric Acid, conc.	Reagent Grade
Silica Gel grade 923, 100-200 mesh	Aldrich Cat.# 21,447-7
Florisil, 100-200 mesh	Fisher Cat.# F101-500
C <sub>18</sub> SPE (3 mL) Bakerbond	J.T. Baker
Sodium Chloride	Fisher Cat.# 5671-3
Sodium Sulfate	Fisher Cat.# 5420-3
Silica Gel (flash column)	Baker Chemical Co., 40 $\mu$ m average particle diameter

2.3 Standard and Standard Stability

Purity 99.7%      Lot# CH 39/169-1  
 Supplied by NISSAN  
 Chemical Industries  
 Agrochemical Division  
 Tokyo, Japan

The standard when in solution (acetonitrile) is stable for at least 3 months when kept at approximately 4°C in the dark. Standard solution stability data is summarized in Table II and is detailed in Table X.

2.4 Standard Solutions for Fortifications

Whenever a set of samples is analyzed, the performance of the method should be tested by simultaneously analyzing samples fortified with known amounts of pyridaben. Control samples are fortified prior to extraction, as indicated within the steps of the method, by the delivery with a volumetric pipet of an aliquot of an analytical standard which provides the desired concentration of pyridaben (e.g. 5 mL of a 0.25  $\mu$ g/mL standard fortified into 25 g of whole orange is equivalent to 0.05 ppm).

Pyridaben(BAS 300 I): the recommended concentrations are 1000, 100, 50, 1  $\mu$ g/mL in acetonitrile. Standard solutions should be stored in amber glass bottles in a refrigerator (approximately 4°C).

#### 2.4 Standard Solutions for Fortifications (cont.)

Prepare a 1000  $\mu\text{g/mL}$  (1 mg/mL) BAS 300 I stock solution by transferring an appropriate amount into a volumetric flask. Dissolve with acetonitrile and dilute to the mark. For example to prepare a 50 mL stock solution, dissolve 50 mg BAS 300 I in a 50 mL volumetric flask with acetonitrile. Dilute to the mark with acetonitrile.

Prepare a 100.0  $\mu\text{g/mL}$  BAS 300 I standard solution by transferring an appropriate amount of the 1000  $\mu\text{g/mL}$  stock solution with a volumetric pipet to a volumetric flask (typically 5 mL of the 1000  $\mu\text{g/mL}$  stock solution into a 50 mL volumetric flask). Dilute to the mark with acetonitrile.

Prepare a 50.0  $\mu\text{g/mL}$  and 1  $\mu\text{g/mL}$  BAS 300 I standard solutions by making an appropriate dilutions or sequential serial dilutions of the 100  $\mu\text{g/mL}$  standard solution and diluting with acetonitrile. Other concentrations may be used as appropriate.

#### 2.5 Standard Solutions for GC Analysis

Pyridaben (BAS 300 I): The recommended concentrations are 5.0, 0.3, 0.2, 0.10 and 0.05  $\mu\text{g/mL}$  in acetonitrile or toluene. Standard solutions should be stored in amber glass bottles in a refrigerator (approximately 4°C).

**Note:** The fortification standards can also be used for GC analysis.

Prepare a 5.0  $\mu\text{g/mL}$  BAS 300 I standard solution by transferring an appropriate amount of the 50  $\mu\text{g/mL}$  standard solution with a volumetric pipet to a volumetric flask (typically 5.0 mL of the 50  $\mu\text{g/mL}$  standard solution into a 50 mL volumetric flask). Dilute to the mark with acetonitrile or toluene.

Prepare a 0.30  $\mu\text{g/mL}$ , 0.2  $\mu\text{g/mL}$ , 0.1  $\mu\text{g/mL}$  and 0.05  $\mu\text{g/mL}$  standard solutions by making appropriate dilutions of the 5.0  $\mu\text{g/mL}$  standard solution and diluting with acetonitrile or toluene. Other concentrations may be used as appropriate.

### 3 Analytical Procedure

The following procedures are for whole orange, whole orange (alternative procedure), orange oil, dried orange pulp, orange molasses, orange peel and orange juice. Flow charts for the various matrices are presented in Figures 1-6.

### 3.1 Preparation of Samples

Homogenize orange and orange processed commodity samples thoroughly before subsampling and weighing. Remove any extraneous material. Depending on the sample consistency, the samples may be homogenized manually (i.e. juice and molasses) or mechanically. Dry ice may be used to aid in this process, but it must be completely sublimed before any sampling is done.

### 3.2 Method for Whole Orange and Orange Juice

#### 3.2.1 Extraction

- a. Weigh 25 g ( $\pm$  0.2 g) of homogenized orange sample into a 250 mL Nalgene centrifuge bottle (fortification samples are fortified at this time).
- b. Add 100 mL of acetone/water (8:2 v/v) to the Nalgene bottle and macerate the sample for 2-3 minutes with a Polytron.
- c. Rinse the Polytron blade with acetone. Collect the rinses in the Nalgene bottle.
- d. Centrifuge the sample at 1000-1500 rpm for 5 minutes. Decant the supernatant liquid into a 1L flat bottom flask.
- e. Add 100 mL of acetone/deionized water (8:2 v/v) to the Nalgene bottle. Shake the bottle to break up pelletized matter. Centrifuge as in step d. and decant the sample into the 1L flask.
- f. Repeat step 3.2.1.e. two additional times for whole orange and one additional time for orange juice and collect all decants in the 1L flask.

#### 3.2.2 Hexane Partition

- a. Add 25 g of NaCl to the acetone/water extract and stir for 5-10 minutes using a magnetic stir bar and stirring plate.
- b. After the acetone and water phases have separated, transfer the contents of the flask to a 500 mL separatory funnel (leaving behind any undissolved NaCl).
- c. Add 100mL of hexane to the 1L flat bottom flask, swirl and add to the separatory funnel (this helps transfer any residues still in flask).
- d. Shake the separatory funnel vigorously and drain the aqueous layer back into the 1L flask.
- e. Drain the hexane/acetone layer into a clean 1L flat bottom flask through a funnel equipped with filter paper and 50 grams of sodium sulfate.
- f. Pour the aqueous layer back into the separatory funnel and extract with an additional 100 mL of hexane.
- g. Discard the aqueous phase and collect the hexane layer in the 1L flask through the same funnel.

### 3.2.3 Hexane/Acetonitrile Partition

- a. Concentrate the hexane/acetone extract to dryness with a rotary evaporator at a water bath temperature  $\leq 55^{\circ}\text{C}$ .

**Note:** It may be necessary to periodically add small amounts of acetonitrile to aid in the evaporation of residual water.

- b. Add 100 mL of acetonitrile. Swirl and sonicate sample to dissolve as much of the matrix as possible.
- c. Add 100 mL of hexane to the flask, swirl and sonicate until virtually all matrix has been dissolved.
- d. Quantitatively transfer the hexane and acetonitrile phases to a 500 mL separatory funnel using two 10 mL acetonitrile rinses.
- e. Shake the separatory funnel vigorously and collect the acetonitrile in a 500 mL flat bottom flask.
- f. Add an additional 100 mL of acetonitrile to the separatory funnel to further extract the hexane layer. Combine both acetonitrile layers and discard the hexane layer.
- g. Concentrate the acetonitrile to near dryness (approximately 5 mL) with a rotary evaporator at a bath temperature of  $\leq 55^{\circ}\text{C}$ .

**Note:** If the sample is allowed to evaporate to dryness, pyridaben will be lost and low recoveries for the fortified samples will result.

- h. Quantitatively transfer residues to a 25 mL volumetric flask using dichloromethane (DCM) washes and dilute to the mark with DCM.

### 3.2.4 Florisil Column Clean-Up

- a. Place a glass wool plug at the lower end of a chromatographic column (11 mm i.d.), close the stopcock and add 10 mL of hexane/ether (9:1 v/v). Slowly pour 5 g of Florisil through a glass funnel into the column. Gentle tap the column to release any trapped air. Lower the meniscus to the Florisil surface.
- b. Transfer a 40% aliquot (10 mL) from the sample in the 25 mL volumetric flask (Section 3.2.3.h) to a 15 mL centrifuge tube and dry the sample under a stream of nitrogen. A bath with a water temperature not exceeding  $50^{\circ}\text{C}$  may be used.

**Note:** It is critical to remove all traces of acetonitrile because this can greatly effect the elution profile during column chromatography.

### 3.2.4 Florisil Column Clean-Up (cont.)

- c. Apply the residues to the column using 3 x 2 mL of hexane/ether (9:1 v/v) rinses. For each rinse, sonicate and/or use a vortex to dislodge any solid material from the tube. All particulate matter may not go into solution. After each rinse is added to the column, the meniscus is lowered to the florisil surface.

Note: If particulate matter is observed, approximately 0.5-1 cm of chromatographic sand can be added to the top of the column prior to adding the sample to avoid clogging of the column.)

- d. Elute the contaminants with 70 mL of hexane/ether (9:1 v/v).
- e. Elute the active ingredient with 150 mL of hexane/ether (9:1 v/v) and collect in a 250 mL flat bottom flask.
- f. Concentrate the eluate to dryness with a rotary evaporator at a water bath temperature of  $\leq 55^{\circ}\text{C}$ . Dilute sample to an appropriate final volume using acetonitrile. The sample is ready for injection.

Note: In analyzing a set of samples, if the movement of a colored band through the florisil is noticeably more with any sample compared to the other samples, this most likely indicates that not all of the acetonitrile was removed in step 3.2.4.b. for that sample and step 3.2.4. must be repeated.

Note: As the activity of Florisil can vary, it is recommended to heat the Florisil at  $110^{\circ}\text{C}$  or greater for 24 hours prior to use. After removing from an oven, the Florisil must be kept in a desiccator no longer than one week prior to use. Also, because the ether used contains a small amount of alcohol (2%), the use of a new lot of this chemical should trigger a check of the elution profile. It is recommended that matrix be included in the evaluation of any profile.

### 3.3 Alternative Procedure for Whole Orange

#### 3.3.1 Extraction

- a. Weigh 25 g ( $\pm 0.2$  g) of homogenized orange sample into a 250 mL glass bottle (fortification samples are fortified at this time).
- b. Add 100 mL of acetone/water (8:2 v/v) to the glass bottle and macerate the sample for 2-3 minutes with a polytron.
- c. Rinse the polytron blade with acetone. Collect the rinses in the glass bottle.

### 3.3.1 Extraction (cont.)

- d. Vacuum filter the slurry through a Buchner funnel (9 cm) containing 1 sheet of Whatman No. 5 (9 cm) and 1 sheet of No. 4 (24 cm) filter paper into a 500 mL filter flask. Place the 9 cm paper in the funnel first followed by the larger filter paper which is pressed down into the filter using a beaker with a diameter less than 9 cm. The larger paper will prevent small particles from clogging the first filter paper. Rinse the filter materials with acetone (stop the vacuum during the wash).
- e. Quantitatively transfer the filtrate to a 500 mL volumetric flask using acetone rinses. Adjust to 500 mL with acetone.

### 3.3.2 DCM Partition

- a. Quantitatively remove 10% (50 mL) of the extract from the previous step and place into a 125 mL flat-bottom flask. Date, label and store the remaining 90% of the extract in a refrigerator (approximately 4°C). Evaporate the aliquot to approximately 25 mL using a rotary evaporator with a water bath temperature of  $\leq 55^{\circ}\text{C}$ .
- b. Add 20 mL of a 10% aqueous NaCl solution (w/v) to the sample.
- c. Transfer the solution into a 125 mL separatory funnel and extract three times each with 25 mL of DCM. For each extraction, shake gently for approximately 30 seconds. Filter each DCM extract through Whatman phase separator paper (1PS) into a 125 mL flat-bottom flask. Rinse the filter paper with DCM (not more than 20 mL) and add this rinse to the flat-bottom flask.
- d. Evaporate the combined DCM extracts to near dryness on a rotary evaporator with a water bath temperature of  $\leq 55^{\circ}\text{C}$  and then to dryness with a gentle stream of nitrogen.

### 3.3.3 Mini-Silica Gel Column Chromatography

- a. Weigh out 1.0 g of silica gel (flash chromatography grade). Transfer the silica gel into an 8 mL glass column with a frit at the bottom and place a glass wool plug (should not be excessive) or a second frit at the top of the silica gel.
- b. Use a SPE vacuum manifold (aspirator) for all the steps with the mini-silica column (solvent flow rate is 11-14 mL/min).
- c. Condition the column by passing 20 mL of dichloromethane (DCM) followed by 20 mL of 30% DCM/hexane through, without allowing the column to go dry.
- d. Add 1.5 mL of DCM to the sample flask from step 3.3.2.d., swirl the flask (or sonicate for 30 second) to dissolve any residues left on the wall of the sample flask. Add 3.5 mL of hexane, swirl the flask and transfer this solution to the conditioned column. Lower the meniscus to the silica gel surface. Collect the eluate in a waste container.

### 3.3.3 Mini-Silica Gel Column Chromatography (cont.)

- e. Rinse the sample flask with 10 mL of hexane followed by 40 mL of 30% DCM/hexane and swirl to dissolve any residues left from the previous step. Add the rinses to the column and collect the eluate in the waste container.
- f. Elute the analyte of interest with 120 mL of 55% DCM/hexane (v/v). Collect the eluate in a 125 mL flat bottom flask.
- g. Evaporate the eluate to approximately 80 mL using a low stream of N<sub>2</sub> and then rotary evaporate with a water bath temperature of ≤40°C to just dryness. Remove traces of the solvent using a low stream of N<sub>2</sub>.
- h. Dissolve the sample in an appropriate volume of toluene for final GC determination and swirl, using a vortex mixer, for 30 seconds. For a 2.5 gram aliquot sample, the control and 0.05 ppm fortification sample should be diluted to the same volume (typically 2 mL). The sample is ready for injection.

### 3.4 Method for Orange Peel

#### 3.4.1 Extraction

- a. Follow the procedure for whole oranges (section 3.2.1).

#### 3.4.2 Hexane Partition

- a. Follow the procedure for the whole oranges (section 3.2.2).

#### 3.4.3 Hexane/Acetonitrile Partition

- a. Follow the procedure for the whole oranges (section 3.2.3)

#### 3.4.4 Silica Column Clean-Up

- a. Transfer a 40% (10 mL) aliquot from the sample in the 25 mL volumetric flask to a 15 mL centrifuge tube and dry the sample under a stream of nitrogen.
- b. Place a glass wool plug at the lower end of a chromatographic column (i.d. 15 mm). Slurry 10 grams of silica gel (100-200 mesh) in DCM and pour into column using a long stemmed funnel. Lower the meniscus to the silica surface.
- c. Apply the residue to the column with 3 x 2 mL DCM rinses. For each rinse, sonicate and/or use a vortex mixer to aid in the transfer.
- d. Elute the contaminants with 40 mL of DCM and collect in a waste container.
- e. Elute the active ingredient with 150 mL of 1% ethyl acetate in DCM (v/v).
- f. Concentrate the eluate to 5 mL with a rotary evaporator at a water bath temperature of ≤55°C and transfer the residues to a 15 mL centrifuge tube using several DCM rinses.
- g. Evaporate to dryness using a stream of nitrogen.

### 3.4.5 C<sub>18</sub> Column Clean-Up

- a. Condition a SPE C<sub>18</sub> column with 10 mL of acetonitrile followed by 10 mL of acetonitrile/water (1:1 v/v) with a 2-4 mL/minute flow rate (use the same rate for all steps).
- b. Dissolve the residue by adding 1 mL of acetonitrile, swirl and then add 1 mL of water to the centrifuge tube and swirl. Transfer onto the column and collect the eluate in a waste container.
- c. Transfer any possible remaining residues with 2 x 2 mL of acetonitrile/water (1:1 v/v) rinses and collect the eluate in the waste container.
- d. Elute the contaminants with 30 mL of acetonitrile/water (1:1 v/v) and collect the eluate in the waste container.
- e. Elute the active ingredient with 15 mL of acetonitrile/water (3:1 v/v) and collect in a 50 mL flat bottom flask.
- f. Concentrate the eluate to dryness with a rotary evaporator at a water bath temperature of  $\leq 55^{\circ}\text{C}$ . Dilute sample to an appropriate final volume using acetonitrile. The sample is ready for injection.

### 3.5 Method for Dried Orange Pulp

#### 3.5.1 Extraction

- a. Weigh 10 g ( $\pm 0.2$  g) into a 250 mL Nalgene centrifuge bottle (fortification samples are fortified at this time).
- b. Add 75 mL of 0.5 N HCl to the bottle and allow the sample to soak for 1 hour.
- c. Add 75 mL of acetone and macerate the sample for 3 minutes with a Polytron.
- d. Rinse the Polytron blade with acetone. Collect the rinses in the Nalgene bottle.
- e. Centrifuge the sample at 1000-1500 rpm for 5 minutes and decant the supernatant into a 1L flat bottom flask.
- f. Add 100 mL of acetone/deionized water (8:2 v/v) to the bottle. Shake the bottle to break up the pelletized material. Centrifuge the sample and decant the supernatant liquid.
- g. Repeat step f. two additional times and collect all decants in the 1L flask.

#### 3.5.2 Hexane Partition

- a. Follow the procedure for whole oranges (section 3.2.2).

#### 3.5.3 Hexane/Acetonitrile Partition

- a. Follow the procedure for whole oranges (section 3.2.3) except for steps g and h.

#### 3.5.4 Silica Column Clean-Up

- a. Evaporate the acetonitrile extract to approximately 5 mL and transfer the residues to a 15 mL centrifuge tube using dichloromethane rinses.
- b. Evaporate to dryness using a stream of nitrogen.
- c. Prepare and run silica gel column as described for orange peels (steps 3.4.4.b. through 3.4.4.g.).

#### 3.5.5 C<sub>18</sub> Column Clean-Up

- a. Follow the C<sub>18</sub> column clean-up procedure for orange peels (section 3.4.5).

### 3.6 Method for Orange Molasses

#### 3.6.1 Extraction

- a. Weigh 10 g ( $\pm 0.2$  g) of orange molasses into a 250 mL Nalgene centrifuge bottle (fortified samples are fortified at this time).
- b. Add 50 mL of 0.5 N HCl followed by 50 mL of acetone to the plastic centrifuge bottle. Macerate the contents for approximately 3 minutes using a polytron.
- c. Rinse the blade with acetone followed by water and collect the rinses in the plastic centrifuge bottle.
- d. Centrifuge the sample at 1000-1500 rpms for approximately 5 minutes. Decant the supernatant liquid into a 1 L flat bottom flask.
- e. Add 20 mL of deionized water followed by 80 mL of acetone to the centrifuge bottle. Shake the bottle after capping to break up the pelletized material.
- f. Centrifuge the sample as described in step d. above and decant the supernatant into the same 1 L flask.
- g. Repeat steps e. and f.

#### 3.6.2 Hexane Partition

- a. Add 35 g of NaCl and 50 mL of distilled water to the acetone/water extract and stir for 5-10 minutes using a magnetic stir bar and stirring plate.
- b. Follow the procedure for whole oranges (steps 3.2.2.b. through 3.2.2.h.).

#### 3.6.3 Hexane/Acetonitrile Partition

- a. Follow the procedure for the whole orange, steps 3.2.3.a through 3.2.3.f.
- b. Concentrate the acetonitrile to approximately 5-10 mL with a rotary evaporator at a water bath temperature of  $\leq 55^{\circ}\text{C}$ , making sure the solution does not go to dryness.

#### 3.6.4 Water/DCM Partition

- a. Add 50 mL of DCM to the sample from step 3.5.3.b. Transfer the solution quantitatively to a 250 mL separatory funnel using DCM rinses.
- b. Rinse the flat bottom flask with 100 mL of 0.5 N HCl, dissolving any remaining residue, if present. Transfer the rinse to the 250 mL separatory funnel.
- c. Shake the funnel and allow the phases to separate. Drain the DCM layer through 1PS phase separation filter paper into a 250 mL flat bottom flask.
- d. Extract the aqueous layer with another 50 mL of DCM and collect through same phase separator paper into the same flask.
- e. Concentrate the DCM to dryness with a rotary evaporator at a water bath temperature of  $\leq 55^{\circ}\text{C}$ .

#### 3.6.5 Silica Column Clean-Up

- a. Prepare and run a silica gel column as described for orange peels (steps 3.4.4.b. through 3.4.4.g.).

#### 3.7 Method for Orange Oil

##### 3.7.1 Extraction

- a. Weigh 5 g ( $\pm 0.2$  g) of orange oil into a 250 mL centrifuge bottle (fortification samples are fortified at this time).
- b. Add 100 mL of hexane and 50 mL of acetonitrile to bottle.
- c. Fix the bottle on mechanical shaker and shake for 10 minutes.
- d. Transfer the solution to a 250 mL separatory funnel and drain the acetonitrile layer into a 250 mL flat bottom flask.
- e. Transfer the hexane layer back into the bottle and repeat extraction procedure with an additional 50 mL of acetonitrile.
- f. Combine the acetonitrile extracts and concentrate to dryness with a rotary evaporator at a water bath temperature of  $\leq 55^{\circ}\text{C}$ .

##### 3.7.2 Florisil Column Clean-Up

- a. Prepare and run a Florisil column as described for whole oranges (section 3.2.4).

##### 3.7.3 C<sub>18</sub> Column Clean-Up

- a. Prepare and run a C<sub>18</sub> column as described for orange peel (section 3.4.5).

### 3.8 Instrumentation

#### 3.8.1. Description of Equipment

The following equipment was used during the validation of this method. Other GC instruments and columns may be used as long as acceptable chromatography, including sensitivity, is obtained.

Gas Chromatograph Hewlett Packard (HP) 5890 Series II with a <sup>63</sup>Ni-electron capture detector, electronic pressure control, HP 7673 autosampler, and HP Cyclo Double Gooseneck Sleeve (4mm id)

Column J & W Scientific DB-5, 15m x 0.32mm id and 1.0 $\mu$ m film thickness

#### 3.8.2. Typical Operating Conditions

The following conditions were used during validation of this method. Other conditions may be used as long as acceptable chromatography is obtained.

##### Temperatures

Injector: 250°C  
Column: 130°C for 0.5 min.,  
ramp at 30°C/min. to 250°C  
hold for 4 min.

##### Alternative:

130°C for 0.5 min.,  
ramp at 30°C/min to 230°C,  
hold for 7.0 min.,  
ramp at 30°C/min to 275°C  
hold for 6.0 min.

Detector: 300°C

##### Gases

Carrier: Helium  
Make Up Gas: Nitrogen  
Constant Column Flow Rate: 8mL/min  
Injection Volume: 1 $\mu$ L or 2 $\mu$ L  
Retention Time: 7.2 min.  
(Alternative) 10.1 min.

### 3.8.3. Calibration Procedures

Calculation of results is based on peak height measurements using a calibration curve. The standard curve is obtained by direct injection of either 1 $\mu$ L or 2 $\mu$ L aliquot of the pyridaben GC analysis standards in the range of 0.05 $\mu$ g/ml to 0.30 $\mu$ g/ml (using at least 3 different concentrations). Alternate concentration ranges can be used depending on the sensitivity of the detector. Plot the log of the peak heights versus the log of the amount of injected standard. Using log transformations should give a linear response. Peak height versus amount may be used for a linear fit as long as the correlation coefficient is greater than 0.98.

### 3.8.4. Sample Analysis

Inject several concentrations of standards to establish the stability of the detection response. For analysis, alternate sample (or groups of samples) and standard (or groups of standards) injections. For each injection set, the set should begin and end with standard injections and each standard level should be injected at least in duplicate.

## 3.9 Interferences

### 3.9.1 Sample Matrices

If interfering peaks from the matrix occur in the chromatogram, change the GC operating conditions (i.e. oven program or column flow rate) or use an alternative GC column.

### 3.9.2 Other Sources

Other Pesticides: Method specificity was carried out using the pesticides registered for use on pome and citrus fruits. The pesticides were scanned through the GC-ECD program used for pyridaben analysis. No pesticides interfered with the determination of pyridaben residues. The pesticides tested are listed in BASF Analytical Method D9312 (see reference 2).

Solvents: None observed to date.

Lab Ware: None observed to date.

## 3.10 Confirmatory Techniques

If peak identity is doubtful, different columns can be used, e.g. DB-17. Also, GC-MSD can be used as a positive confirmatory technique. Typical GC/MS chromatograms of standard, control, and fortified samples are presented in Appendix B.

### 3.10.1 Description of Equipment

**Instrument:** A model 5970 mass selective detector from Hewlett Packard. The instrument is automatically and manually tuned once a week for maximum sensitivity (for ion m/z 219) using perfluorotributylamine. Detection by selected ion monitoring (SIM) at m/z 365 ( $M^+$ ) and 309 ( $M^+ - C_4H_7$ ). The dwell time is one second. The gas chromatograph (model 5890, series II form Hewlett Packard) is connected to the MSD with a capillary interface kept at 280°C.

**Column:** J & W DB-17 (50% diphenyl, 50% dimethyl polysiloxane), 30 m, 0.32 mm (ID) and 0.5  $\mu$ m film thickness.

### 3.10.2 Operating Conditions

**Gases:**

Carrier	Ultra-high purity (99.999%) Helium
Head Pressure	10 psi
Flow Rate	4 mL/min.

**Oven Program:**

Initial	150°C
Ramp	45°C/min to 280°C, hold 10 min.

**Injection:** Splitless with solenoid valve open after 1 min. 2-3mL/min. septum purge 280°C Injection temperature

**Retention Time:** 10.2 min.

### 3.11 Time Required for Analysis

The time required for a set of 4 samples, 2 recoveries and 2 controls is 16 hours. For the alternative whole orange procedure, the time required is 8 hours. This includes the analytical procedure, GC injection, evaluation and reporting, provided that no special problems arise, such as matrix interferences.

### 3.12 Potential Problems and Helpful Hints

During work-up, samples may be stored at any step in the method except those which leave the samples dissolved in dichloromethane. Storage in dichloromethane should be avoided. During storage overnight, samples should be refrigerated (approximately 4°C).

During large analytical sets, the detector sensitivity can vary due to matrix effects. Solvent rinse vials should be placed after each concentrated sample (final volume < 10 mL) injected if this problem arises.

### 3.12 Potential Problems and Helpful Hints (cont.)

In order to provide column stability during the course of an injection set, it is recommended to condition the column with injections of concentrated samples (final volume < 10 mL) intermittent with standard injections prior to the start of the set. Once the standard response has leveled off to an acceptable level, then the set may be started.

As the performance of solid phase extraction sorbents can vary from lot to lot, it is highly recommended to check the column performance of any new lot with a pyridaben standard, preferably dissolved in control matrix extract. If necessary, the elution mixture or volume may be adjusted.

It is highly recommended for all column clean-up procedures that preluates are stored until success of an analysis is confirmed. In the case where low recoveries for fortification samples result, the preluate may be examined for residues.

## 4 METHODS OF CALCULATION

### 4.1 Principle

Calculation of results is based on peak height measurements. The amount of pyridaben in injected samples ( $W_A$ ) is determined from the calibration curve and the equation described in section 4.2 is utilized for the determination of residue (R). The calculation can also be made by a suitable computer program.

At least one fortification and one untreated sample (= control) are run with each set of samples. The amount of pyridaben for fortification samples should be on the order of magnitude of the expected residue or lower. The recovery (= B) is determined as described in section 4.3.

### 4.2 Calculation of Residues

The residue of pyridaben (R) in ppm is calculated as follows (example calculation given in Figure 7):

$$R = \frac{W_A}{G} \times \frac{V_E}{V_I} \times \frac{1}{A} \times \frac{1}{1000}$$

R - Residue in ppm

$W_A$  - Amount of pyridaben (in pg) determined from the calibration curve

G - Sample weight in g

$V_E$  - Final volume of the extract before injection (in mL)

$V_I$  - Actual injected volume (in  $\mu$ L) from final volume  $V_E$

A - aliquot

#### 4.3 Calculation of Recoveries

The fortification recovery for pyridaben (B) in % is calculated from the recovery trials as follows (example calculation given in Figure 8):

$$B(\%) = \frac{R_F - R_C}{F} \times 100\%$$

$R_F$  - Fortified sample residue in ppm determined according to calculation in 4.2

$R_C$  - Control sample residue in ppm determined according to calculation in 4.2

$F$  - Amount of active ingredient (in ppm) fortified

### 5 RESULTS AND DISCUSSION

#### 5.1 General

The analytical procedure detailed in this report was validated with representative control samples of each matrix fortified with the test substance over a range of concentrations. Control samples from two magnitude of the residue studies were the sources of the material for the validation analyses. The whole oranges were from BASF study number 92173 (RCN 92256) which is a crop field trial study. The process fractions were from BASF study number 92168 (RCNs 92252 and 92253) which is a processed food/feed study. Representative GC chromatograms of analyses of selected control and fortified samples for each matrix are shown in the appendix. No matrix peaks interfered with the proper quantitation of any recovery samples. Any peak within control samples at the retention time of interest was well below the level of the quantitation limit. Standard curves were generated from standard pyridaben solutions injected concurrently with the analysis set. Typical standard chromatograms along with a typical standard curve are presented in Appendix B.

#### 5.2 Accuracy and Precision

Subsamples of each matrix were fortified at levels from 0.05 ppm (the quantitation limit) to 5.0 ppm with pyridaben and were analyzed by Method D9309. Individual data is presented in Tables III-IX. The accuracy and precision of the validation data were acceptable for all matrices at all levels. Statistical treatment of the data included determination of an average and standard deviation for each matrix and the results are presented in Table I. The molasses data contained statistically more deviation than the data from the other matrices. This is due to the presence of three outlying data points (56, 66, and 49% recoveries) which if discounted change the average recovery from  $81 \pm 15\%$  to  $85 \pm 12\%$ . The average recovery for all matrices was  $86 \pm 10\%$  (N=144).

Essential to the method is the acetone/water extraction of the orange matrices. This procedure is based upon the results generated in the Nature of the Residue Study conducted on oranges treated with Pyridaben (see reference 3).

### 5.3 Quantitation Limit

The quantitation limit for pyridaben residues in orange matrices using Method D9309 is 0.05 ppm. At this level, control samples are relatively clean and good recoveries are obtainable. This is the lowest level which is proven by recovery data.

### 5.4 Ruggedness Testing

For each matrix, two analysts produced the validation data and consistent results were obtained between them. The method will be independently validated by a contract laboratory, and the results issued in a separate report.

### 5.5 Limitations

None known to date.

## 6 CONCLUSIONS

This analytical procedure is applicable for measuring residues of pyridaben in whole oranges, orange peel, orange juice, dried orange pulp, orange molasses, and orange oil down to a level of 0.05 ppm.

The raw data and final method pertaining to this study are maintained in the BASF Agricultural Research Center Archives.

## 7 SAFETY AND HEALTH CONSIDERATIONS

### 7.1 General

Use personal protective equipment such as lab coats, safety glasses and gloves (nitrile/latex gloves are recommended) when performing the operations described in this method. Conduct all filtration, partitions, nitrogen-stream evaporations and SPE procedures in a well-ventilated area. Guard vacuum equipment, such as rotovaps, to minimize the possibility of injury caused by flying broken glass. Dispose of hazardous wastes in an environmentally acceptable manner, in compliance with applicable laws and regulations.

### 7.2 Solvents, Reagents and Standards

Review the Material Safety Data Sheets (MSDSs) for all solvents used in this method. An MSDS for pyridaben can be obtained from BASF Corporation.

## 8 CHANGES TO THE PROTOCOL

Nine changes to the protocol were made during the study. These changes are listed in Appendix A.

9     REFERENCES

1.     Tilting, N.   GC Method for the Determination of Pyridaben in Plants. Method 938/1. BASF Report No. 2832. September, 1991.
2.     Abdel-Baky, S.   Method for Determination of Residues of Pyridaben in Apple and Apple Processed Commodities by Gas Chromatography. BASF Method No. D9312. March 1994.
3.     Singh, M.   Nature of the Residue of <sup>14</sup>C-BAS 300I in Citrus. BASF Report No. M9215. January 1994. BASF Registration Document No. 94/5011.

10 SIGNATURES

We, the undersigned, hereby declare that this study was performed under our supervision according to the procedures described herein, and that this progress report provides a true and accurate record of the results obtained.

Author: D. Scott Malinsky Date: April 7, 1994  
D. Scott Malinsky

Author: Samy Abdel-Baky Date: April 5, 1994  
Samy Abdel-Baky

Study Director/Author: Jeffrey D. Burkey Date: April 7, 1994  
Jeffrey D. Burkey

Approved By: Robert C. Paulick Date: March 24 1994  
Robert C. Paulick, Ph.D.  
Group Leader, Analytical

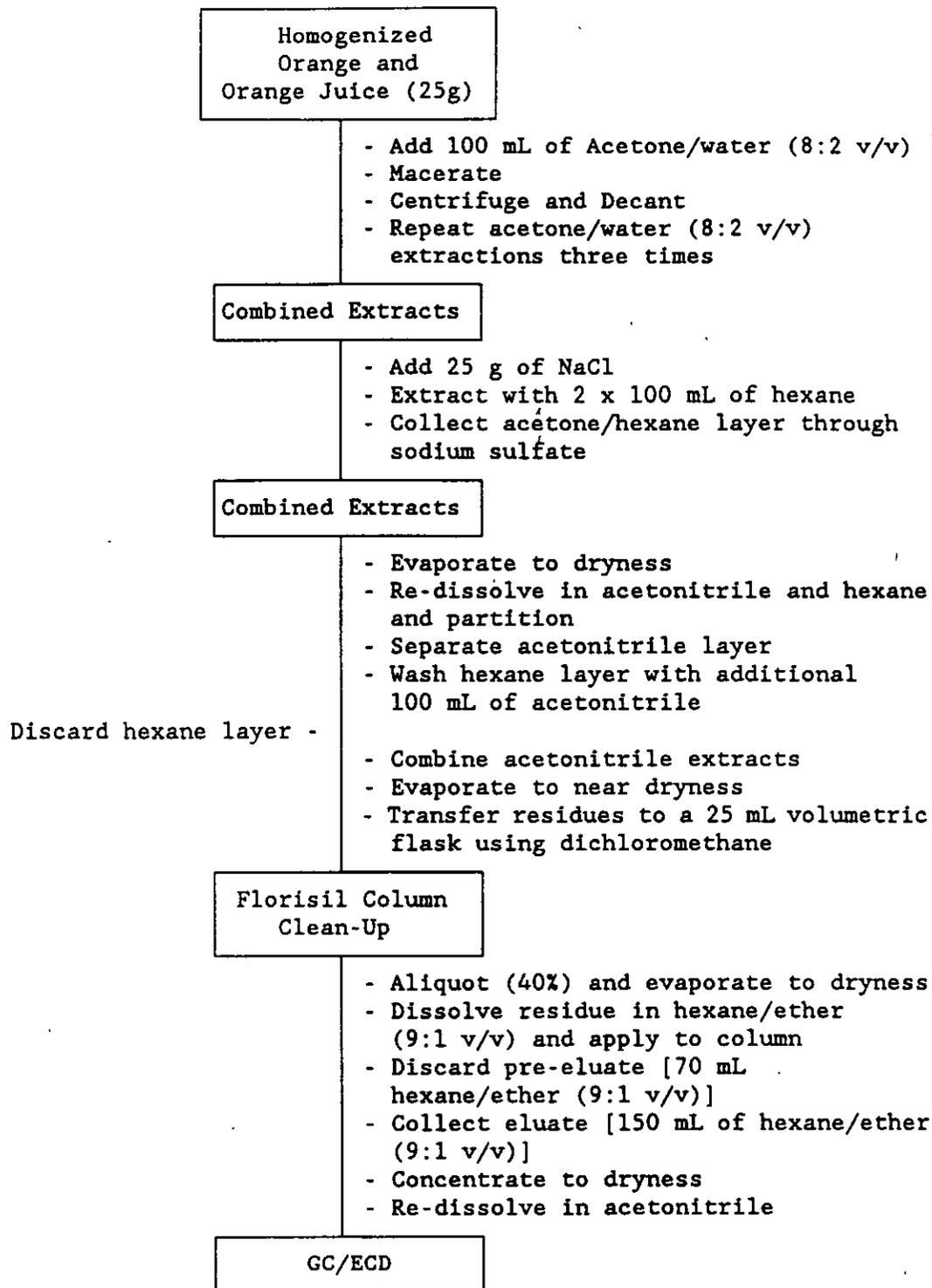


Figure 1. Whole Orange and Orange Juice Analytical Procedure.

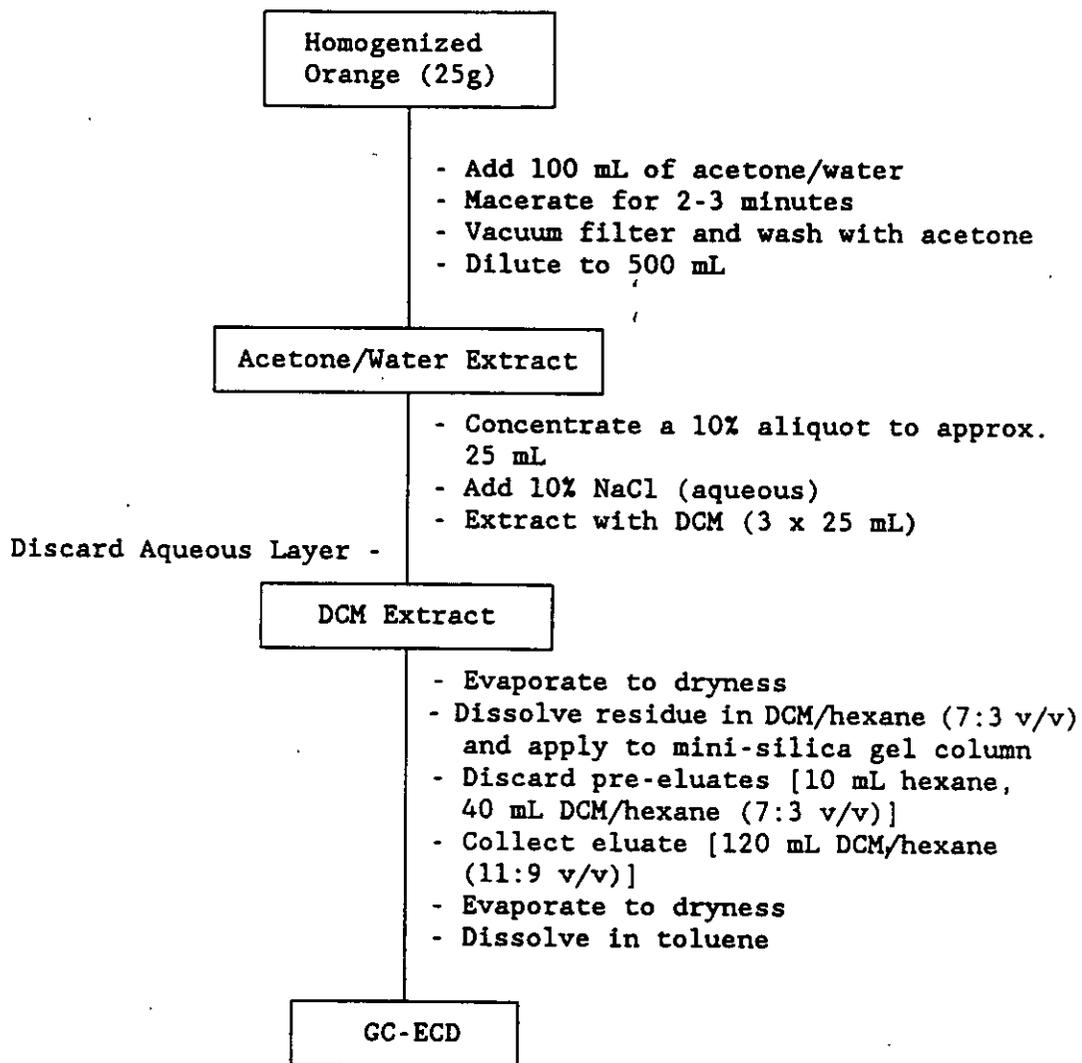


Figure 2. Whole Orange Alternative Analytical Procedure.

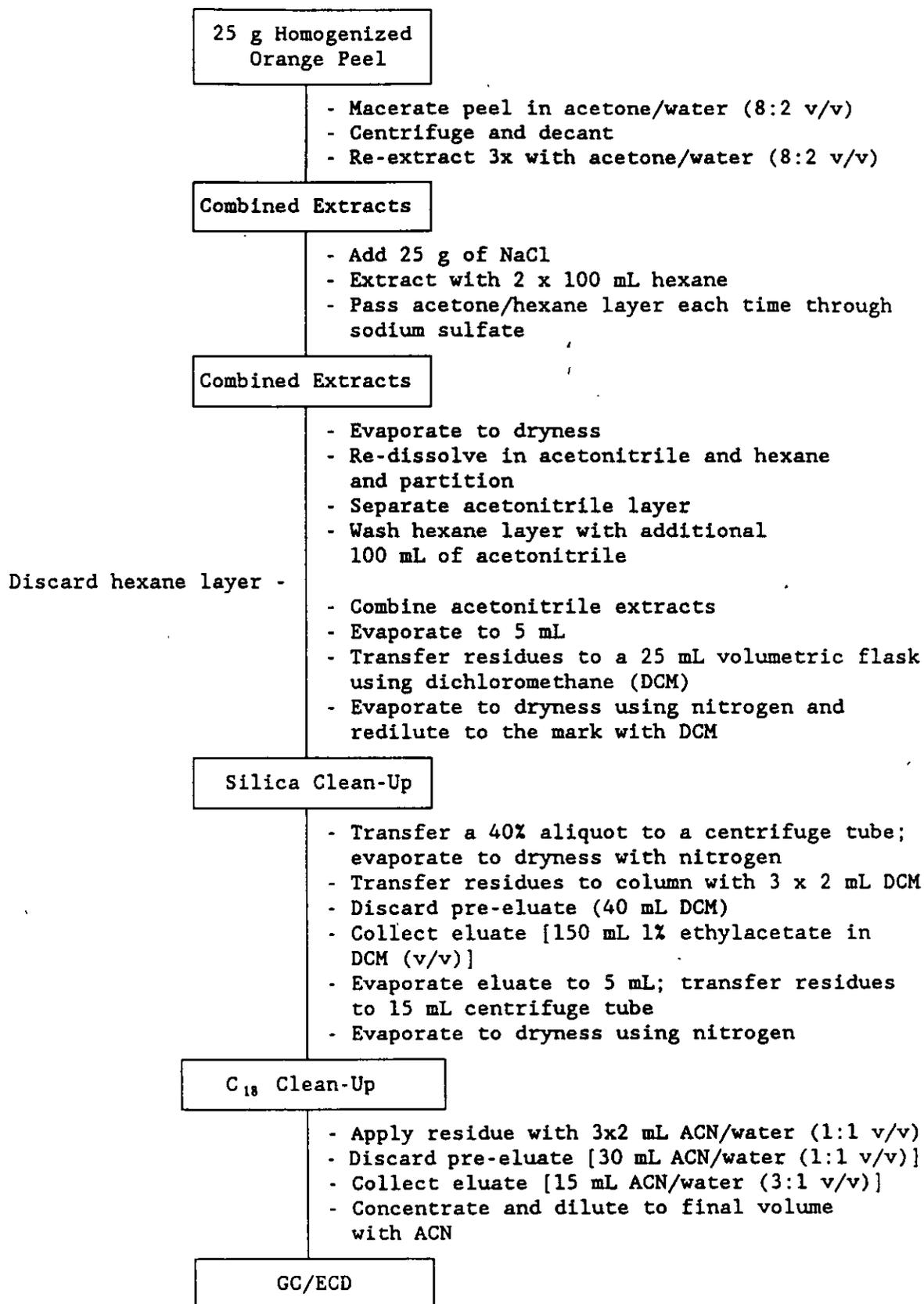


Figure 3. Orange Peel Analytical Procedure

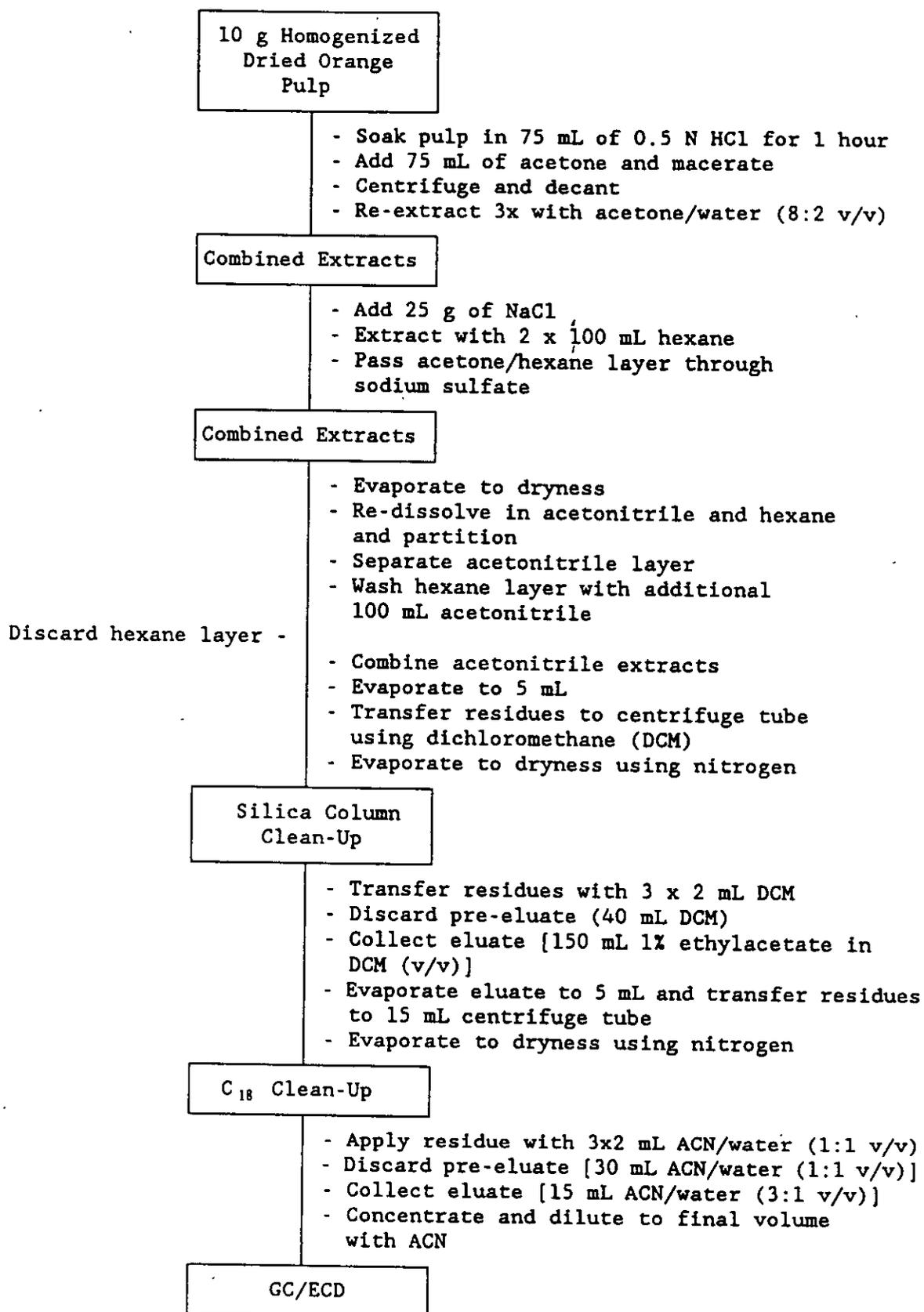


Figure 4. Dried Orange Pulp Analytical Procedure

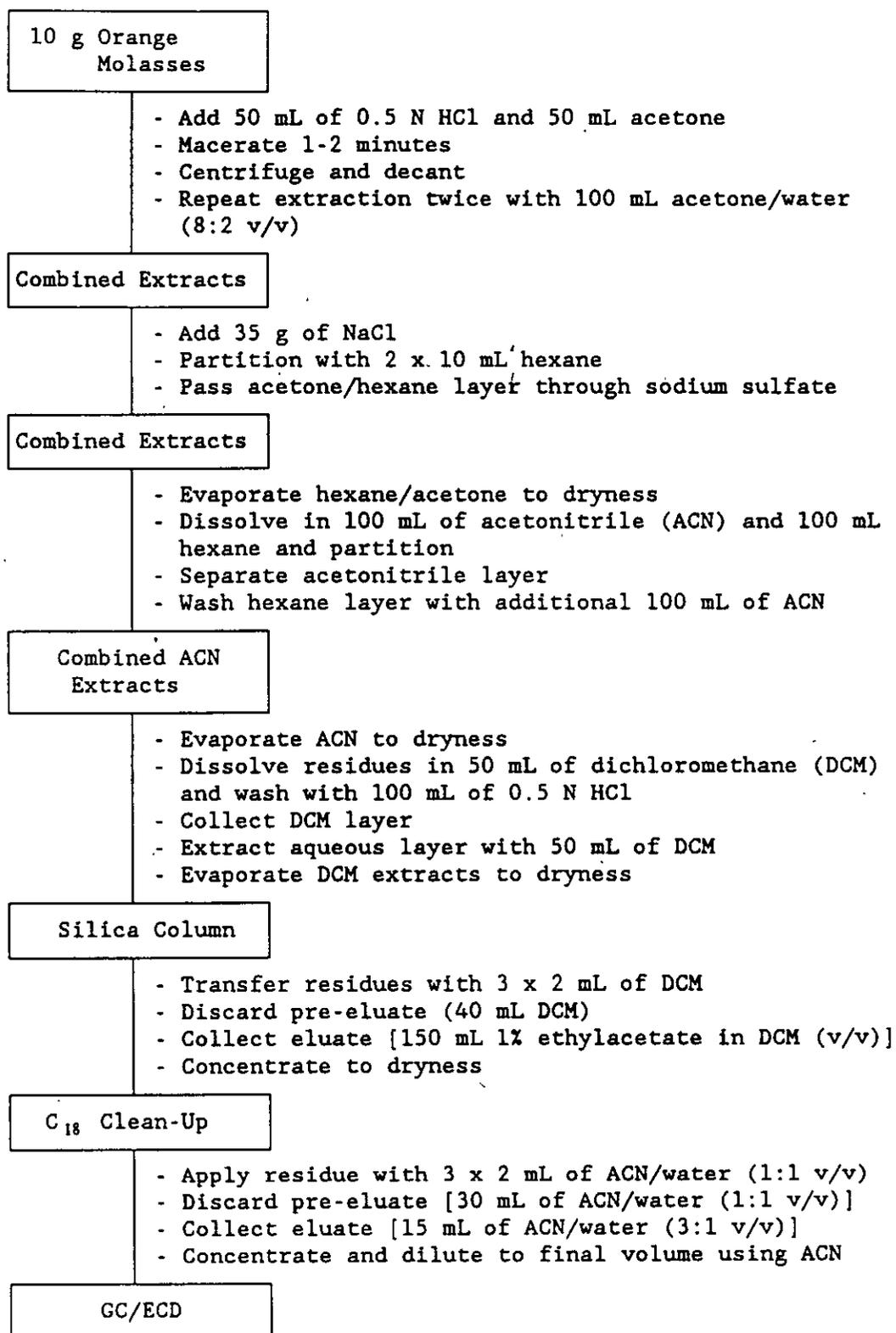


Figure 5. Orange Molasses Analytical Procedure

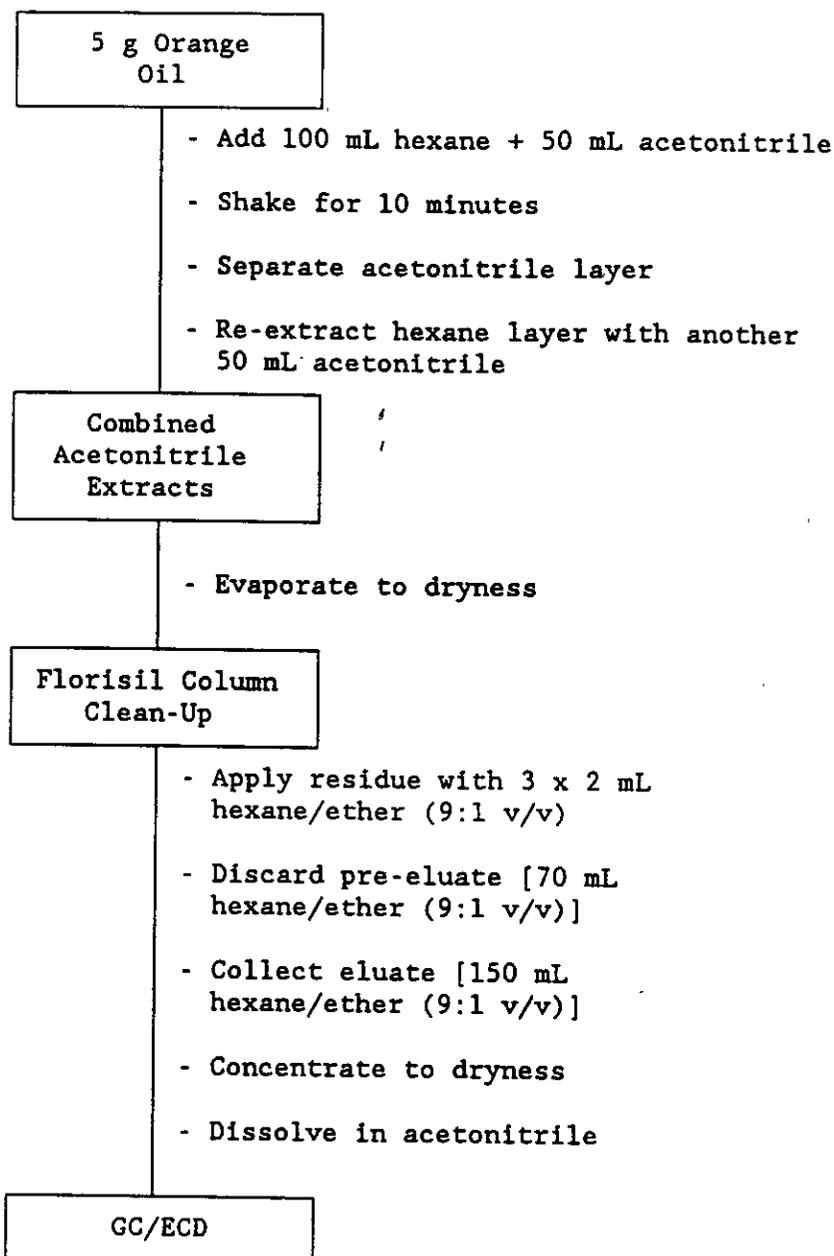


Figure 6. Orange Oil Analytical Procedure.

Lab Sample Number 190275, Control Whole Orange Fortified with 0.05 ppm of Pyridaben (BAS 300I).

Residue (ppm of BAS 300I) -

$$\frac{\text{BAS 300I Found (pg)}}{\text{Sample Weight (g)}} \times \frac{\text{Final Volume (mL)}}{\text{Injection Volume (\mu L)}} \times \frac{1}{\text{Aliquot}} \times \frac{1}{1000}$$

Sample Weight	-	25.0 g
Final Volume	-	5.0 mL
Injection Volume	-	1 $\mu$ L
Aliquot	-	0.40

To determine BAS 300I found (pg):

a. If the Y-axis is log height and X-axis is log amount, then:

$$\text{BAS 300I found (pg)} = 10^{[\log(\text{peak height}) - \text{intercept}] \cdot \text{slope}}$$

b. If the Y-axis is log amount and X-axis is log height:

$$\text{BAS 300I found (pg)} = 10^{[\text{slope} \cdot \log(\text{peak height}) + \text{intercept}]}$$

Example of (b) is:

$$\text{BAS 300I found (pg)} = 10^{[1.299 \cdot \log(7020) + (-2.887)]} = 129 \text{ pg}$$

$$\text{Residue} = \frac{129 \text{ pg}}{25.0 \text{ g}} \times \frac{5.0 \text{ mL}}{1 \mu\text{L}} \times \frac{1}{0.40} \times \frac{1}{1000} = 0.0645 \text{ ppm}$$

Peak Height - 7020

Slope (Master Sheet 93102-1) - 1.299

Intercept (Master Sheet 93102-1) - -2.887

Note: The standard curve for pyridaben was generated using a linear fit of the log transformations of the peak height and BAS 300I found.

Lab Sample Number 190275, Control Whole Orange Fortified with 0.05 ppm of Pyridaben (BAS 300I).

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Recovery (%)	-	$\frac{\text{BAS 300I Found (ppm)}}{\text{BAS 300I Fortified (ppm)}} \times 100\%$
BAS 300I Fortified	-	0.05 ppm
BAS 300I Found	-	Fortified Sample Residue (ppm) - Control Sample Residue (ppm)
Residue (ppm)	-	Calculated according to equations shown in Figure 7.
Sample weight	-	25.0 g
Final Volume	-	5.0 mL (Fortified and Control Samples)
Injection Volume	-	1 $\mu$ L
Aliquot	-	0.40
Peak Height	-	7020 (Fortified) (2614) (Control, approximated by extrapolation)
Slope	-	1.299 (Master Sheet 93102-1)
Intercept	-	-2.887 (Master Sheet 93102-1)
Fortified Sample Residue	-	0.0645
Control Sample Residue	-	0.0179
BAS 300I Found	-	0.0645 - 0.0179 = 0.0466 ppm
Recovery	-	$\frac{0.0466}{0.05} \times 100\% = 93\%$

Figure 8. Typical Recovery Calculation

TABLE I. Summary of Validation Data for Pyridaben (BAS 300I) in Oranges and Orange Processed Commodities

Matrix	Fortification Level (ppm)	Number of Analyses	Standard Deviation ( $\pm$ %)	Average Recovery (%)
Whole Oranges	0.05	6	7	86
	0.50	6	6	87
	5.0	6	7	90
	Overall	18	7	87
Whole Oranges (Alternative Method)	0.05	9	5	84
	0.50	9	5	84
	5.0	9	5	85
	Overall	27	5	85
Peel	0.05	6	12	97
	0.50	6	3	90
	5.0	6	9	88
	Overall	18	9	92
Juice	0.05	6	5	94
	0.50	6	4	96
	5.0	6	4	94
	Overall	18	4	95
Dried Pulp	0.05	6	4	86
	0.50	6	6	86
	5.0	6	11	84
	Overall	18	7	86
Molasses	0.05	9	13	88
	0.50	9	16	83
	5.0	9	14	73
	Overall	27	15	81
Oil	0.05	6	5	81
	0.50	6	8	85
	5.0	6	7	83
	Overall	18	7	83
Overall	0.05 - 5.0	144	10	86

TABLE II. Summary of Analytical Standard Solution Stability Data for Pyridaben

Storage Period (Months)	Recovery (%)
Pyridaben 1 mg/mL acetonitrile	
0	104
1	103
2	103
3	101
Pyridaben 0.10 µg/mL in acetonitrile	
0	105
1	104
2	102
3	100

- During storage, standards were refrigerated at approximately 4°C in amber glass bottles.

TABLE III. Individual Validation Data for Whole Oranges

Fortification Level (ppm)	Master Sheet No. (A93102-)	Lab Sample Number	Peak Height <sup>1,2</sup> ( $\mu$ V)	Final Volume (mL)	Residue <sup>3</sup> (ppm)	Recovery <sup>4</sup> %
0.00	1	109273	(1997)	5	<0.05	--
0.00	1	109274	(2614)*	5	<0.05	--
0.00	2	109317	(1890)	5	<0.05	--
0.00	2	109318	(2259)*	5	<0.05	--
0.05	1	109275	7020	5	0.065	93
0.05	1	109276	6881	5	0.063	90
0.05	1	109277	7008	5	0.064	93
0.05	2	109319	6555	5	0.053	79
0.05	2	109320	7413	5	0.054	82
0.05	2	109321	6435	5	0.051	77
0.5	1	109278	9357	25	0.468	90
0.5	1	109279	9374	25	0.469	90
0.5	1	109280	9484	25	0.477	92
0.5	2	109322	9621	25	0.434	84
0.5	2	109323	10881	25	0.446	87
0.5	2	109324	8926	25	0.393	76
5.0	1	109281	9543	250	4.80	96
5.0	1	109282	9349	250	4.68	93
5.0	1	109283	9542	250	4.80	96
5.0	2	109325	8924	250	3.93	78
5.0	2	109326	9457	250	4.24	85
5.0	2	109327	9971	250	4.54	91

- 1 Values within parentheses signify that the peak signal was at a level below the level of the lowest standard.
- 2 For the control samples (0.00 ppm fortification), if an asterisk (\*) appears after the peak height value, corresponding fortification samples from the same master sheet were corrected for this control residue.
- 3 Residues were determined according to the calculations given in Figure 7.
- 4 Recoveries were determined according to the calculations given in Figure 8.

The following values were constant for all analyses

- a. Sample size was 25.0 g
- b. Injection volume was 1  $\mu$ L
- c. Aliquot was 0.40

TABLE IV. Individual Validation Data for Whole Oranges - Alternative Procedure

Fortification Level (ppm)	Master Sheet No. (A93102-)	Lab Sample Number	Peak Height <sub>1</sub> (μV)	Final Volume (mL)	Residue <sup>2</sup> (ppm)	Recovery <sup>3</sup> (%)
0.00	24	3	ND	2	<0.05	--
0.00	24	5	ND	2	<0.05	--
0.00	25	3	(3382) <sup>4</sup>	2	<0.05	--
0.00	25	5	(3343) <sup>4</sup>	2	<0.05	--
0.00	26	3	(3583) <sup>5</sup>	2	<0.05	--
0.00	26	5	(3003) <sup>5</sup>	2	<0.05	--
0.05	24	8	7313	2	0.039	79
0.05	24	10	7655	2	0.042	83
0.05	24	13	7175	2	0.039	77
0.05	25	8	10907	2	0.061	93
0.05	25	11	10428	2	0.058	86
0.05	25	14	10354	2	0.058	85
0.05	26	8	9846	2	0.055	80
0.05	26	11	10386	2	0.058	87
0.05	26	14	10282	2	0.057	85
0.50	24	15	13005	10	0.383	77
0.50	24	18	13658	10	0.406	81
0.50	24	19	13971	10	0.417	83
0.50	25	17	14606	10	0.435	84
0.50	25	20	14715	10	0.439	85
0.50	25	23	14232	10	0.421	81
0.50	26	17	14552	10	0.435	84
0.50	26	20	15770	10	0.478	93
0.50	26	23	15610	10	0.473	92
5.0	24	22	14005	100	4.18	84
5.0	24	23	13744	100	4.09	82
5.0	24	26	13325	100	3.94	79
5.0	25	26	14358	100	4.26	85
5.0	25	28	14204	100	4.20	84
5.0	25	30	13925	100	4.11	82
5.0	26	26	15025	100	4.51	90
5.0	26	28	14787	100	4.43	88
5.0	26	30	15554	100	4.71	94

- 1 Values for control samples (0.00 ppm fortification level) which are listed as ND had no signal detected by the computer integrator. Values within parentheses signify that the peak signal was at a level below the level of the lowest standard.
- 2 Residues were determined according to the calculations given in Figure 7.
- 3 Recoveries were determined according to the calculations given in Figure 8.
- 4 The average response from lab sample numbers 3 and 5 from master sheet number 25 was used to determine the control residue to correct the fortification samples from the same master sheet.
- 5 The average response from lab sample numbers 3 and 5 from master sheet number 26 was used to determine the control residue to correct the fortification samples from the same master sheet.

The following values were constant for all analyses:

- a. Sample size was 25.0 g
- b. Injection volume was 2 μL
- c. Aliquot was 0.10

TABLE V. Individual Validation Data for Orange Peel

Fortification Level (ppm)	Master Sheet No. (A93102-)	Lab Sample Number	Peak Height <sup>1</sup> ( $\mu$ V)	Final Volume (mL)	Residue <sup>2</sup> (ppm)	Recovery <sup>3</sup> (%)
0.00	5	109587	ND	5	<0.05	--
0.00	5	109588	ND	5	<0.05	--
0.00	10	110022	ND	5	<0.05	--
0.00	10	110023	ND	5	<0.05	--
0.05	5	109589	6191	5	0.048	96
0.05	5	109590	6226	5	0.049	97
0.05	5	109591	7370	5	0.060	120
0.05	10	110024	7286	5	0.046	93
0.05	10	110025	6937	5	0.043	87
0.05	10	110026	7129	5	0.045	90
0.50	5	109592	10446	25	0.462	93
0.50	5	109593	10125	25	0.445	89
0.50	5	109594	10497	25	0.465	93
0.50	10	110027	11319	25	0.424	85
0.50	10	110028	11816	25	0.449	90
0.50	10	110029	11657	25	0.441	88
5.0	5	109595	8445	250	3.55	71
5.0	5	109596	10233	250	4.51	90
5.0	5	109597	10866	250	4.86	97
5.0	10	110030	11765	250	4.47	89
5.0	10	110031	11735	250	4.45	89
5.0	10	110032	12025	250	4.60	92

- 1 Values for control samples (0.00 ppm fortification level) which are listed as ND had no signal detected by the computer integrator.
- 2 Residues were determined according to the calculations given in Figure 7.
- 3 Recoveries were determined according to the calculations given in Figure 8.

The following values were constant for all analyses

- a. Sample size was 25.0 g
- b. Injection volume was 1  $\mu$ L
- c. Aliquot was 0.40

TABLE VI. Individual Validation Data for Orange Juice

Fortification Level (ppm)	Master Sheet No. (A93102-)	Lab Sample Number	Peak Height <sup>1</sup> ( $\mu$ V)	Final Volume (mL)	Residue <sup>2</sup> (ppm)	Recovery <sup>3</sup> (%)
0.00	7	109901	ND	5	<0.05	--
0.00	7	109902	ND	5	<0.05	--
0.00	11	110175	ND	5	<0.05	--
0.05	7	109903	7179	5	0.049	98
0.05	7	109904	6916	5	0.047	93
0.05	7	109905	7182	5	0.049	98
0.05	11	110177	6740	5	0.045	90
0.05	11	110178	6557	5	0.044	87
0.05	11	110179	7106	5	0.049	97
0.50	7	109906	12247	25	0.502	101
0.50	7	109907	12297	25	0.505	101
0.50	7	109908	11846	25	0.480	96
0.50	11	110180	11542	25	0.467	93
0.50	11	110181	11246	25	0.451	90
0.50	11	110182	11691	25	0.475	95
5.0	7	109909	12234	250	5.02	100
5.0	7	109910	11653	250	4.70	94
5.0	7	109911	11383	250	4.55	91
5.0	11	110183	11274	250	4.52	90
5.0	11	110184	11398	250	4.59	92
5.0	11	110185	11724	250	4.77	95

- 1 Values for control samples (0.00 ppm fortification level) which are listed as ND had no signal detected by the computer integrator.
- 2 Residues were determined according to the calculations given in Figure 7.
- 3 Recoveries were determined according to the calculations given in Figure 8.

The following values were constant for all analyses

- a. Sample size was 25.0 g
- b. Injection volume was 1  $\mu$ L
- c. Aliquot was 0.40

TABLE VII. Individual Validation Data for Dried Orange Pulp

Fortification Level (ppm)	Master Sheet No. (A93102-)	Lab Sample Number	Peak Height <sup>1</sup> ( $\mu$ V)	Final Volume (mL)	Residue <sup>2</sup> (ppm)	Recovery <sup>3</sup> (%)
0.00	14	3	ND	5	<0.05	--
0.00	14	5	ND	5	<0.05	--
0.00	22	3	ND	5	<0.05	--
0.00	22	5	ND	5	<0.05	--
0.05	14	8	8237	5	0.041	82
0.05	14	10	8332	5	0.042	83
0.05	14	13	9061	5	0.046	92
0.05	22	8	5089	5	0.042	84
0.05	22	10	5182	5	0.043	86
0.05	22	13	5358	5	0.045	90
0.50	14	15	15183	25	0.424	85
0.50	14	18	16270	25	0.460	92
0.50	14	19	16493	25	0.468	94
0.50	22	15	9100	25	0.423	85
0.50	22	18	8664	25	0.399	80
0.50	22	19	8820	25	0.408	82
5.0	14	22	12225	250	3.28	66
5.0	14	23	15460	250	4.33	87
5.0	14	26	14198	250	3.92	78
5.0	22	22	9924	250	4.70	94
5.0	22	23	9759	250	4.60	92
5.0	22	26	9519	250	4.47	89

- 1 Values for control samples (0.00 ppm fortification level) which are listed as ND had no signal detected by the computer integrator.
- 2 Residues were determined according to the calculations given in Figure 7.
- 3 Recoveries were determined according to the calculations given in Figure 8.

The following values were constant for all analyses

- a. Sample size was 10.0 g
- b. Injection volume was 1  $\mu$ L
- c. No Aliquot

TABLE VIII. Individual Validation Data for Orange Molasses

Fortification Level (ppm)	Master Sheet No. (A93102-)	Lab Sample Number	Peak Height <sup>1</sup> ( $\mu$ V)	Final Volume (mL)	Residue <sup>2</sup> (ppm)	Recovery <sup>3</sup> (%)
0.00	12	110237	ND	5	<0.05	--
0.00	12	110238	ND	5	<0.05	--
0.00	15	110253	ND	5	<0.05	--
0.00	15	110254	ND	5	<0.05	--
0.00	20	3	ND	5	<0.05	--
0.00	20	5	ND	5	<0.05	--
0.05	12	110239	4859	5	0.055	109
0.05	12	110240	4606	5	0.051	102
0.05	12	110241	4442	5	0.049	97
0.05	15	110255	4072	5	0.034	68
0.05	15	110256	4553	5	0.039	78
0.05	15	110257	4773	5	0.041	82
0.05	20	8	4601	5	0.040	79
0.05	20	10	4973	5	0.044	87
0.05	20	13	4944	5	0.043	87
0.50	12	110242	7767	25	0.505	101
0.50	12	110243	7833	25	0.511	102
0.50	12	110244	7689	25	0.499	100
0.50	15	110258	7414	25	0.351	70
0.50	15	110259	8018	25	0.386	77
0.50	15	110260	7759	25	0.371	74
0.50	20	15	6008	25	0.279	56
0.50	20	18	8072	25	0.406	81
0.50	20	19	8572	25	0.439	88
5.0	12	110245	6921	250	4.34	87
5.0	12	110246	6990	250	4.40	88
5.0	12	110247	6782	250	4.23	85
5.0	15	110261	8110	250	3.91	78
5.0	15	110262	6027	250	2.73	55
5.0	15	110263	7339	250	3.47	69
5.0	20	22	7657	250	3.80	76
5.0	20	23	6937	250	3.35	67
5.0	20	26	5438	250	2.45	49

- 1 Values for control samples (0.00 ppm fortification level) which are listed as ND had no signal detected by the computer integrator.
- 2 Residues were determined according to the calculations given in Figure 7.
- 3 Recoveries were determined according to the calculations given in Figure 8.

The following values were constant for all analyses

- a. Sample size was 25.0 g
- b. Injection volume was 1  $\mu$ L
- c. Aliquot was 0.40

TABLE IX. Individual Validation Data for Orange Oil

Fortification Level (ppm)	Master Sheet No. (A93102-)	Lab Sample Number	Peak Height <sup>1,2</sup> ( $\mu$ V)	Final Volume (mL)	Residue <sup>3</sup> (ppm)	Recovery <sup>4</sup> (%)
0.00	16	3	(1253)*	2	<0.05	--
0.00	16	5	(1504)	2	<0.05	--
0.00	21	3	(1555)*	2	<0.05	--
0.00	21	5	(1684)	2	<0.05	--
0.05	16	8	5503	2	0.046	78
0.05	16	10	5543	2	0.047	79
0.05	16	13	5281	2	0.044	74
0.05	21	8	6059	2	0.051	85
0.05	21	10	6067	2	0.051	85
0.05	21	13	6070	2	0.051	85
0.50	16	15	4170	25	0.403	79
0.50	16	18	4048	25	0.388	76
0.50	16	19	4206	25	0.408	80
0.50	21	15	4832	25	0.469	92
0.50	21	18	4837	25	0.469	92
0.50	21	19	4870	25	0.474	93
5.0	16	22	7394	125	4.21	84
5.0	16	23	7165	125	4.04	81
5.0	16	26	6305	125	3.43	69
5.0	21	22	7732	125	4.38	87
5.0	21	23	7867	125	4.48	89
5.0	21	26	7749	125	4.39	88

- 1 Values within parentheses signify that the peak signal was at a level below the level of the lowest standard.
- 2 For the control samples (0.00 ppm fortification), if an asterisk (\*) appears after the peak height value, corresponding fortification samples from the same master sheet were corrected for this control residue.
- 3 Residues were determined according to the calculations given in Figure 7.
- 4 Recoveries were determined according to the calculations given in Figure 8.

The following values were constant for all analyses

- a. Sample size was 5.0 g
- b. Injection volume was 1  $\mu$ L
- c. No Aliquot

TABLE X. Individual Analytical Standard Solution Storage Stability Data for Pyridaben

Storage Period (Month)	Residue Sample No. (93907-)	BASF Standard Number (93-)	Peak Height ( $\mu\text{V}$ )	Recovery <sup>1</sup> (%)
1.0 mg/mL <sup>2</sup>				
0	07	1219	6209	104
1	05	1065	6185	103
2	03	970	6183	103
3	01	821	6090	101
0.10 $\mu\text{L/mL}$				
0	08	1228	6282	105
1	06	1067	6243	104
2	04	972	6136	102
3	02	823	6035	100

- 1 Recoveries were determined by comparison of the peak heights versus the standard data for master sheet number 93102-27 given in Table XI. Because the injection volume was 1  $\mu\text{L}$ , 100% recovery would have been equivalent to 100 pg.
- 2 1.0 mg/mL solutions were diluted to a 0.10  $\mu\text{L/mL}$  concentration prior to injection.

TABLE XI. Summary of Standard Data

Master Sheet Number	Peak Height (uv)				Calibration/Curve Data <sup>1</sup>	
	50pg	100pg	200pg	300pg	Slope	Intercept
1	3315	5545	9483	13062	1.299	-2.887
	3377	5803	9979	13450		
	3524	5868	10115	13817		
2	3791	6064	9843	14232	1.301	-2.943
	3600	6191	10721	14797		
	3817	6557	11378	15180		
5	3821	6433	10918	15177	1.247	-2.743
	3554	6286	11390	15681		
	3585	6462	11300	14978		
7	4217	6951	12209	13408	1.344	-3.193
	4359	7577	12755	17133		
	4517	7525	12891	17186		
10	4698	7466	12436	16837	1.365	-3.305
	4467	7673	12680	17225		
	4753	7947	13182	17510		
11	4333	7163	11601	16181	1.348	-3.205
	4450	7241	12458	16373		
	4379	7076	12476	16818		
12	2733	4603	8065	11235	1.310	-2.791
	2770	4715	7088	10032		
	2555	4394	7792	10233		
14	5255	8849	16664	24504	0.84127	2.30570
	5606	10015	18192	25064		
	5599	9861	17834	24157		
15	3185	5461	10109	14067	1.218	-2.565
	3284	5570	10211	13632		
	3153	5485	9853	13624		
20	3128	5372	9351	13164	0.78224	2.17753
	3182	5698	9464	12839		
	3293	5607	9562	13131		
21	2989	5111	8554	11631	0.75270	2.19983
	2975	5127	8650	11628		
	3032	5102	8331	11540		
22	3108	5595	10245	14451	0.83181	2.10533
	3389	6031	10791	14755		
	3401	5994	10549	14530		
24	3487	6919	13194	18493	0.86191	2.14669
	4317	7780	13839	19058		
	4391	7877	13893	19098		
25	4286	7753	13657	18478	0.83222	2.21947
	4182	7537	13635	18903		
	4327	7880	14080	19207		
26	4035	7669	13550	18570	0.83750	2.20566
	4178	7614	13601	18933		
	4425	7842	13789	19158		
27	3191	6030	11344	16056	0.90315	1.97844
	3227	6099	11623	16394		
	3309	6224	11546	16398		

<sup>1</sup>The formulas for the calibration curves are:

- a.  $\log \text{pg BAS 300 I} = [\text{slope} \times \log (\text{peak height})] + \text{intercept}$
- b.  $\log \text{peak height} = [\text{slope} \times \log (\text{pg BAS 300 I})] + \text{intercept}$

**APPENDIX A**

**Deviations and Amendments to the Protocol**

Protocol changes are listed below:

1. A new lot of pyridaben was defined for use in the study.
2. The extraction procedures for the orange juice and molasses were modified to reduce the number of re-extractions of the marc.
3. The modifications for molasses listed in change 2 were disregarded and a new procedure was defined for the entire molasses procedure.
4. The extraction procedure for dried orange pulp was modified to include using an acidic aqueous solution.
5. The cleanup procedure for orange oil was modified to include a C<sub>18</sub> cleanup. Also, an additional source for control orange oil was specified.
6. The details for the alternative whole orange analysis procedure were defined and the confirmatory technique was defined.
7. Modifications to the alternative whole orange analysis procedure were listed.
8. A deviation from the protocol was defined. For the analytical standard storage stability test, samples were analyzed once instead of in triplicate.
9. A deviation from the protocol was defined. Two technical modifications performed during the validation were accidentally not detailed by amendment. Also, the statement in the protocol detailing what changes to the draft method had to be detailed by amendment was clarified.

Note: All modified procedures were detailed in the final method.

**APPENDIX B**

**Typical Raw Data and Chromatograms**

Description

Figure 1	Typical GC parameters.
Figure 2-5	Typical GC standard chromatograms.
Figure 6	Typical GC standard curve.
Figure 7-13	Typical control and fortified whole orange samples.
Figure 14-20	Typical control and fortified whole orange samples (alternative procedure).
Figure 21-30	Typical control and fortified orange peel samples.
Figure 31-40	Typical control and fortified orange juice samples.
Figure 41-50	Typical control and fortified dried orange pulp samples.
Figure 51-60	Typical control and fortified orange molasses samples.
Figure 61-70	Typical control and fortified orange oil samples.
Figure 71	Typical GC/MS standard chromatogram.
Figure 72-75	Typical control and fortified whole orange samples (GC/MS)

Figure 1. Typical GC parameters.

Study No. 93102

Master Sheet No. 9310224

Date: 10-8-93

Initial: *EMV*

GC Information

Instrument No. 18

GC Model: Varian HP 5890

Injector Temperature: 250 °C Detector Temperature: 300 °C

Detector Type: ECD

Range: 0

Attenuation: 0

Gas flow:

Make-up: 50 psi Air: 0 mL/min

Hydrogen: mL/min Head Pressure: 21.5 psi

Column flow rate: 8.08 mL/min

Column:

Column Phase: DB-5

Serial No. 1172034

Length: 15.0m

Column ID: 0.32 mm

Film thickness: 1.0µm

Oven Program:

Int. Temperature: 130 Initial Hold Time: 0.50 Int. Rate 30 °C/min

Temp. Program 1: 230 Hold Time 1: 7.0 Rate 1 30 °C/min:

Temp. Program 2: 275 Hold Time 2: 6.0 Rate 2 30 °C/min:

Temp. Program 3: Hold Time 3: Rate 3 °C/min:

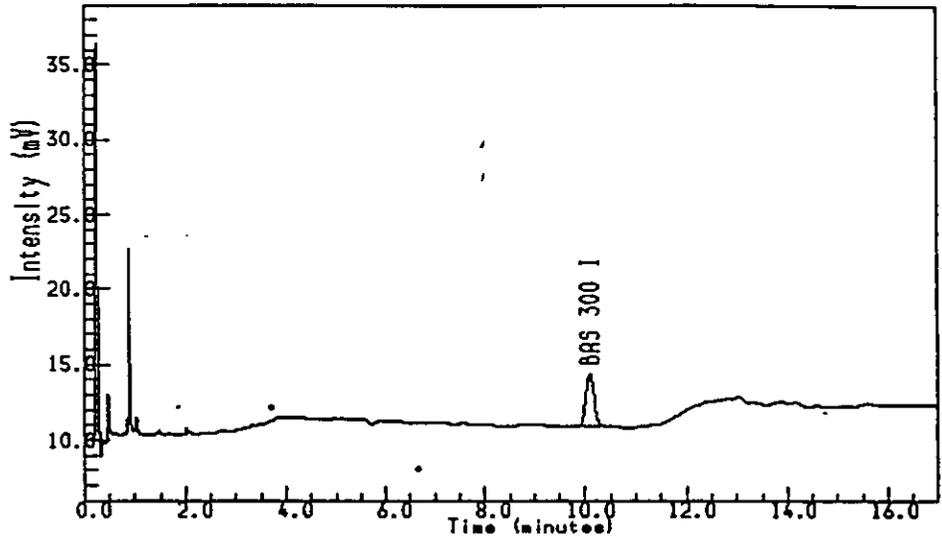
Temp. Program 4: Hold Time 4: Rate 4 °C/min:

Injection Volume: 2.0 µL

Comments:

Figure 2. Typical chromatogram of a 50 pg standard of BAS 300 I. See Table XI, Master Sheet 93102-24.

Acquired on 8-OCT-1993 at 09:08



BASF CORP. - VAX MULTICHROM

Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 50 PG STD  
 Sample Id :  
 Sample Type : Standard Amount=1.00000  
 Bottle No : 1

PEAK INFORMATION

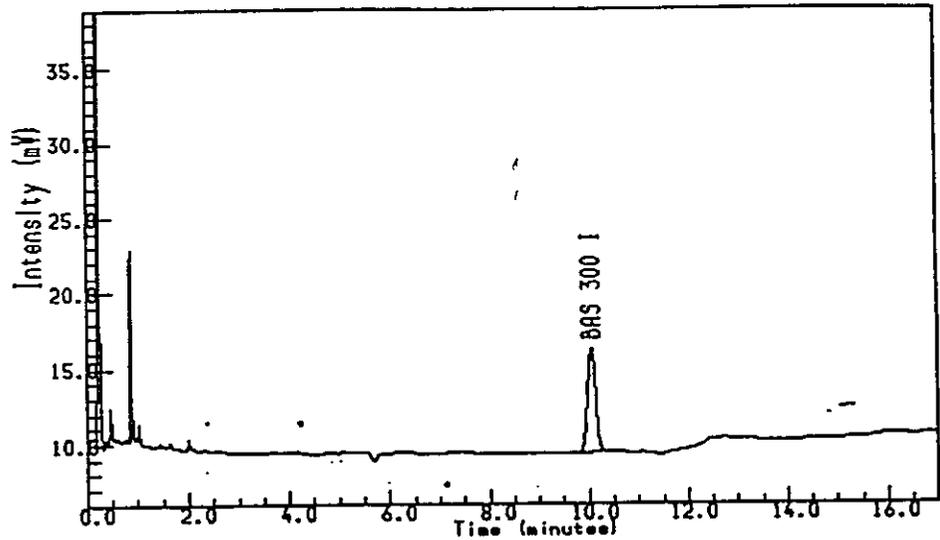
RT mins	Hght uV	ppb	Peak name
10.101	3487	41.630	BAS 300 I

Totals

Unknowns	0	N/A
	3487	41.630
	3487	41.630

Figure 3. Typical chromatogram of a 100 pg standard of BAS 300 I. See Table XI, Master Sheet 93102-24.

Acquired on 8-OCT-1993 at 09:30



BASF CORP. - VAX MULTICHROM

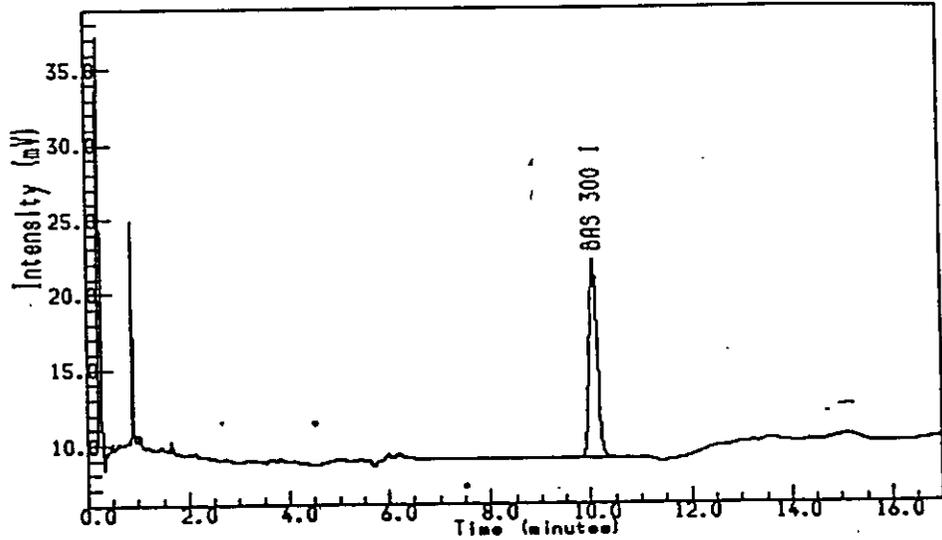
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 100 PG STD  
 Sample Id :  
 Sample Type : Standard Amount=1.00000  
 Bottle No : 2

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.059	6919	92.179	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	6919	92.179	
	6919	92.179	

Figure 4. Typical chromatogram of a 200 pg standard of BAS 300 I. See Table XI, Master Sheet 93102-24.

Acquired on 8-OCT-1993 at 11:18



BASF CORP. - VAX MULTICHROM

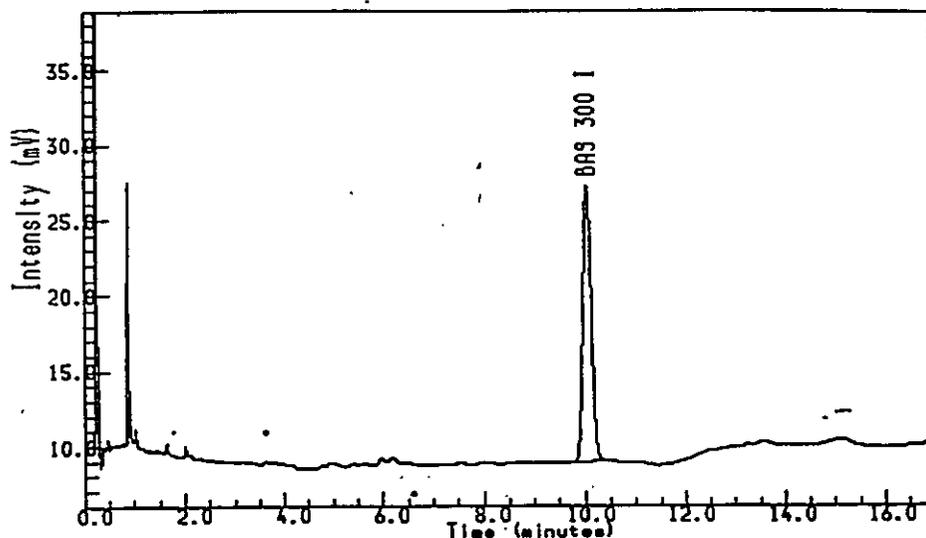
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 200 PG STD  
 Sample Id :  
 Sample Type : Standard Amount=1.00000  
 Bottle No : 7

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.075	13194	194.938	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	13194	194.938	
	13194	194.938	

Figure 5. Typical chromatogram of a 300 pg standard of BAS 300 I. See Table XI, Master Sheet 93102-24.

Acquired on 8-OCT-1993 at 13:06



BASF CORP. - VAX MULTICHROM

Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 300 PG STD  
 Sample Id :  
 Sample Type : Standard Amount=1.00000  
 Bottle No : 11

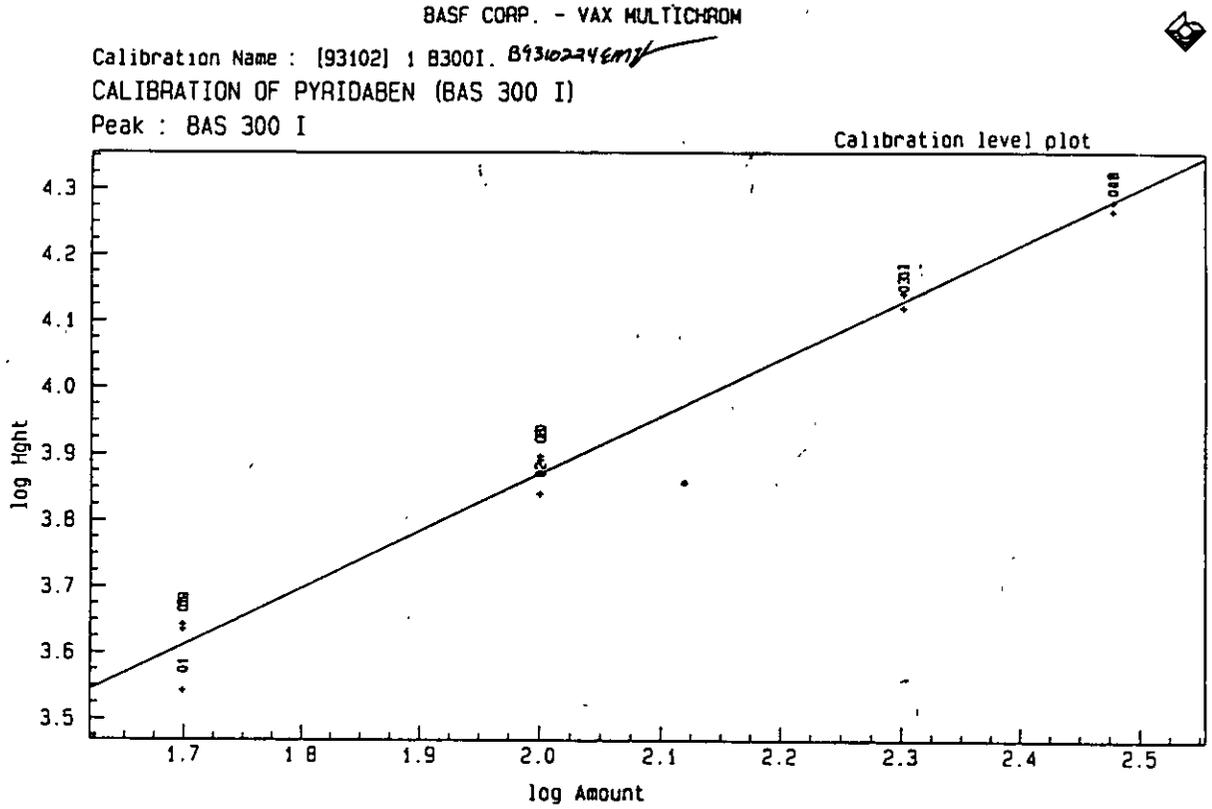
PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.064	18493	288.405	BAS 300 I

Totals

Unknowns	0	N/A
	18493	288.405
	18493	288.405

Figure 6. Typical standard curve for 50, 100, 200, and 300 pg amounts of BAS 300 I. Log transformations of the x-axis and y-axis enabled a linear fit of the data. See Table XI, Master Sheet 93102-24.



Constant : 2.14669  
1st degree : 0.86191

Curve fit : Linear  
Correlation coefficient : 0.99438  
Standard error : 0.02982  
Reported on 11-OCT-1993 at 07:57

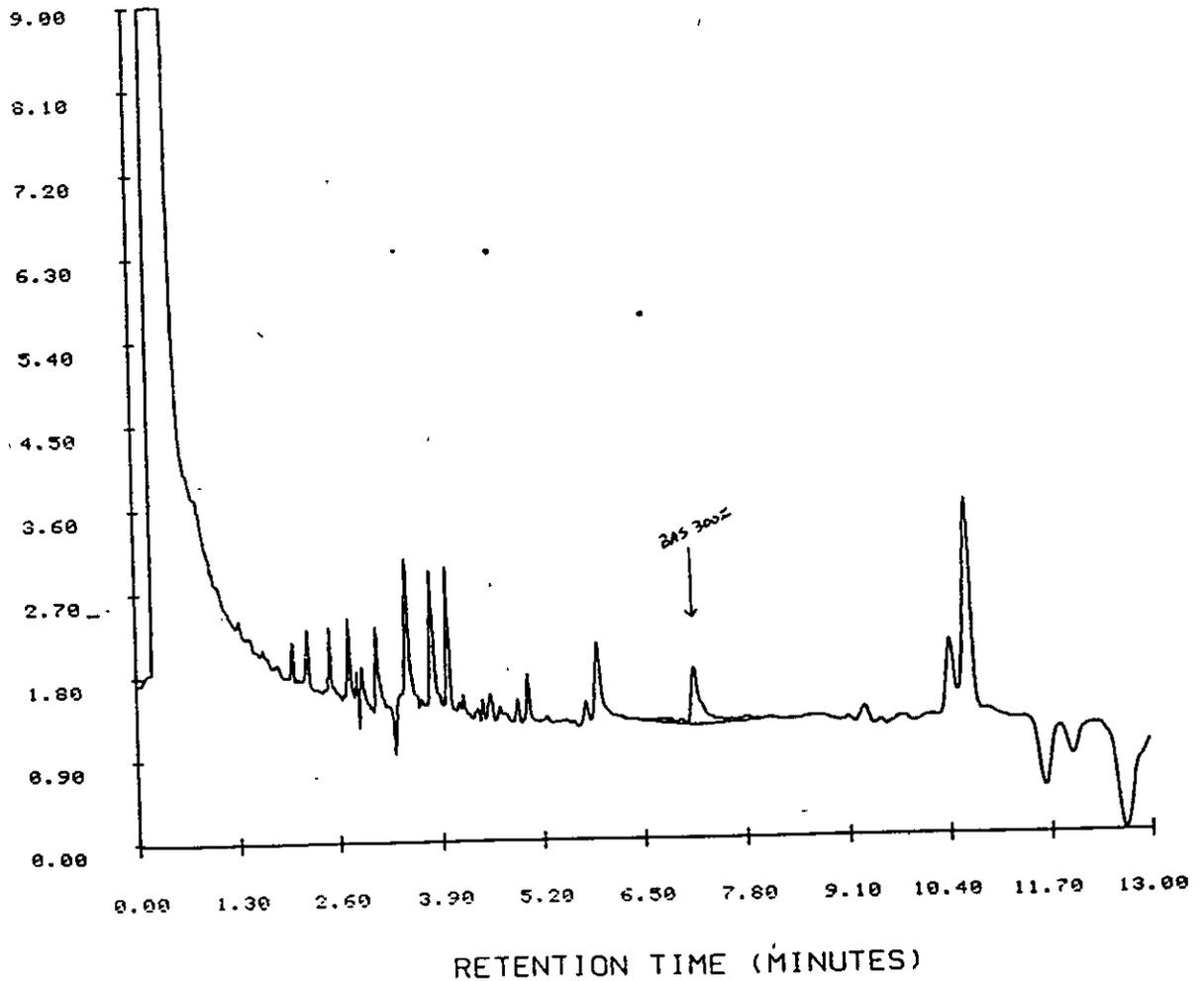
Figure 7.

Chromatogram of a control whole orange sample. Master Sheet 93102-1, Sample Number 109274. See Table III.

### CONTROL B ORANGE

SAMPLE NO.: 109274 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 07/19/93 04:58:42  
PAGE NO.: 01



Y MAXIMUM: 56425.  
Y MINIMUM: 52622.

START TIME: 0.00  
END TIME: 13.00

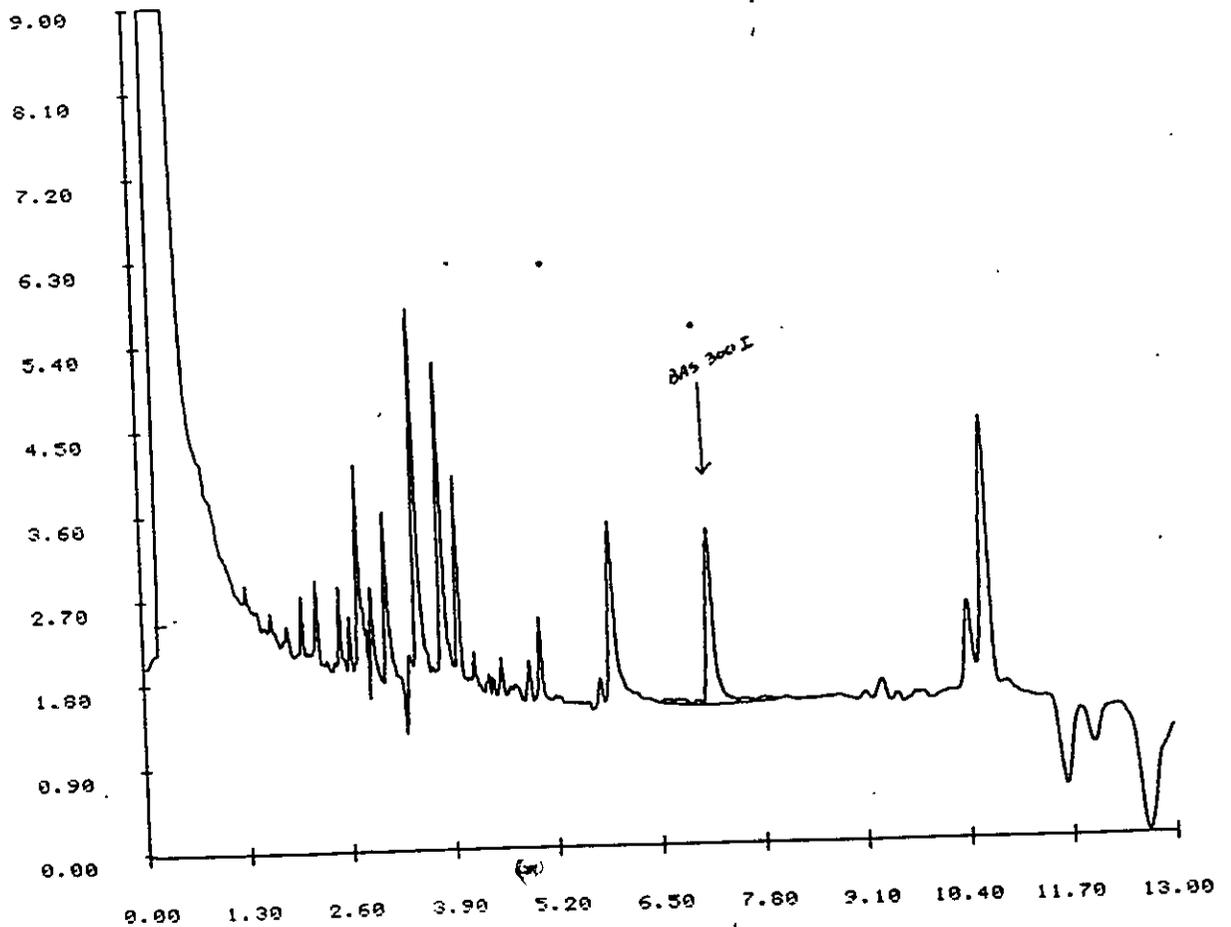
Figure 8.

Chromatogram of a control whole orange sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-1, Sample Number 109275. See Table III.

### 0.05 PPM A ORANGE

SAMPLE NO.: 109275 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 07/19/93 05:32:19  
PAGE NO.: 01



RETENTION TIME (MINUTES)

Y MAXIMUM: 55950.  
Y MINIMUM: 52597.

START TIME: 0.00  
END TIME: 13.00

Figure 9. Chromatogram of a control whole orange sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-1, Sample Number 109276. See Table III.

N625-1026

3C

091

PERKIN-ELMER CORP. PART NO. N625-1026

### 0.05 PPM B ORANGE

SAMPLE NO.: 109276 .01

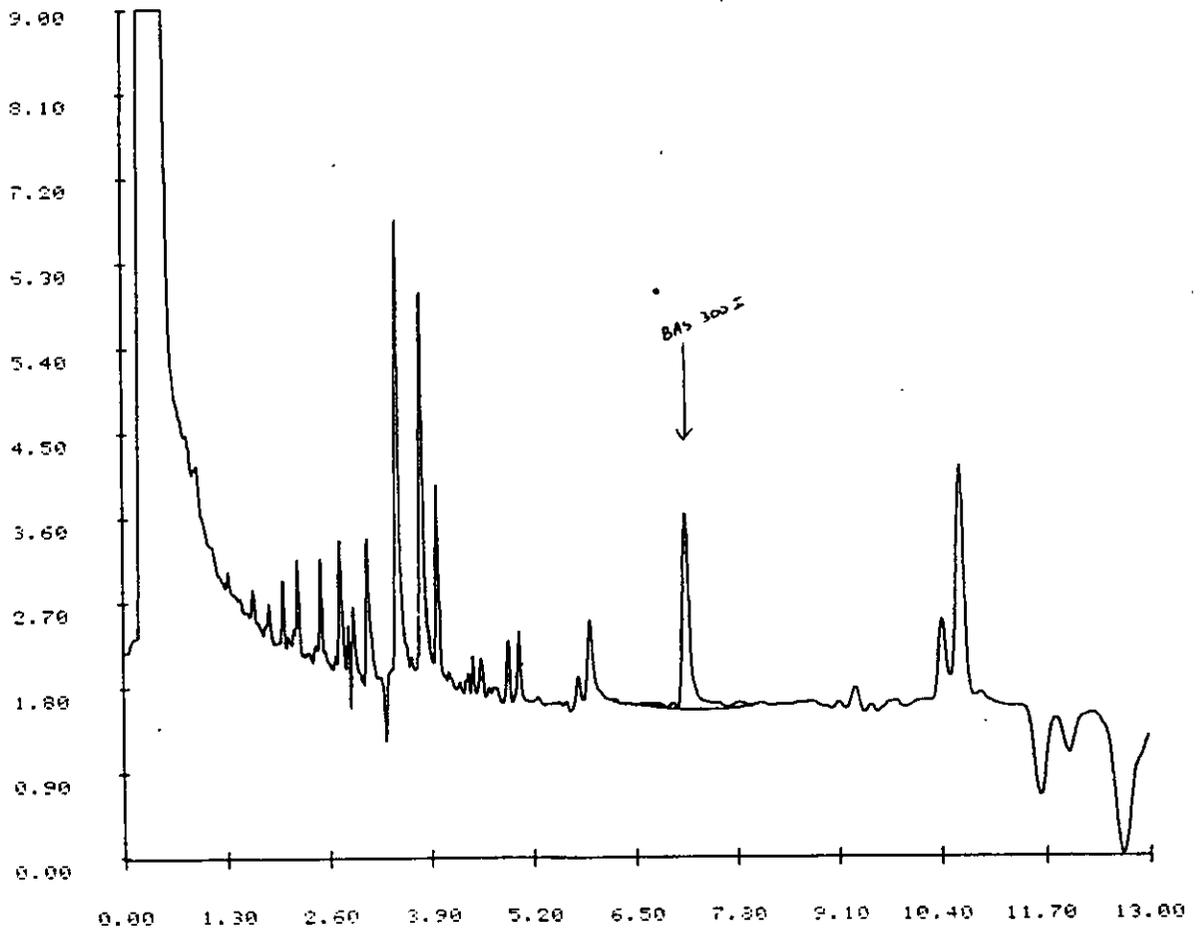
INSTRUMENT: 19

TEST NO.: B3001

DATE TIME: 07/19/93 06:05:51

METHOD NO.: B3001 / B3001

PAGE NO.: 01



RETENTION TIME (MINUTES)

Y MAXIMUM: 55554.

START TIME: 0.00

Y MINIMUM: 52591.

END TIME: 13.00

Figure 10.

Chromatogram of a control whole orange sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-1, Sample Number 109278. See Table III.

### 0.50 PPM A ORANGE

SAMPLE NO.: 109278 .01

INSTRUMENT: 19

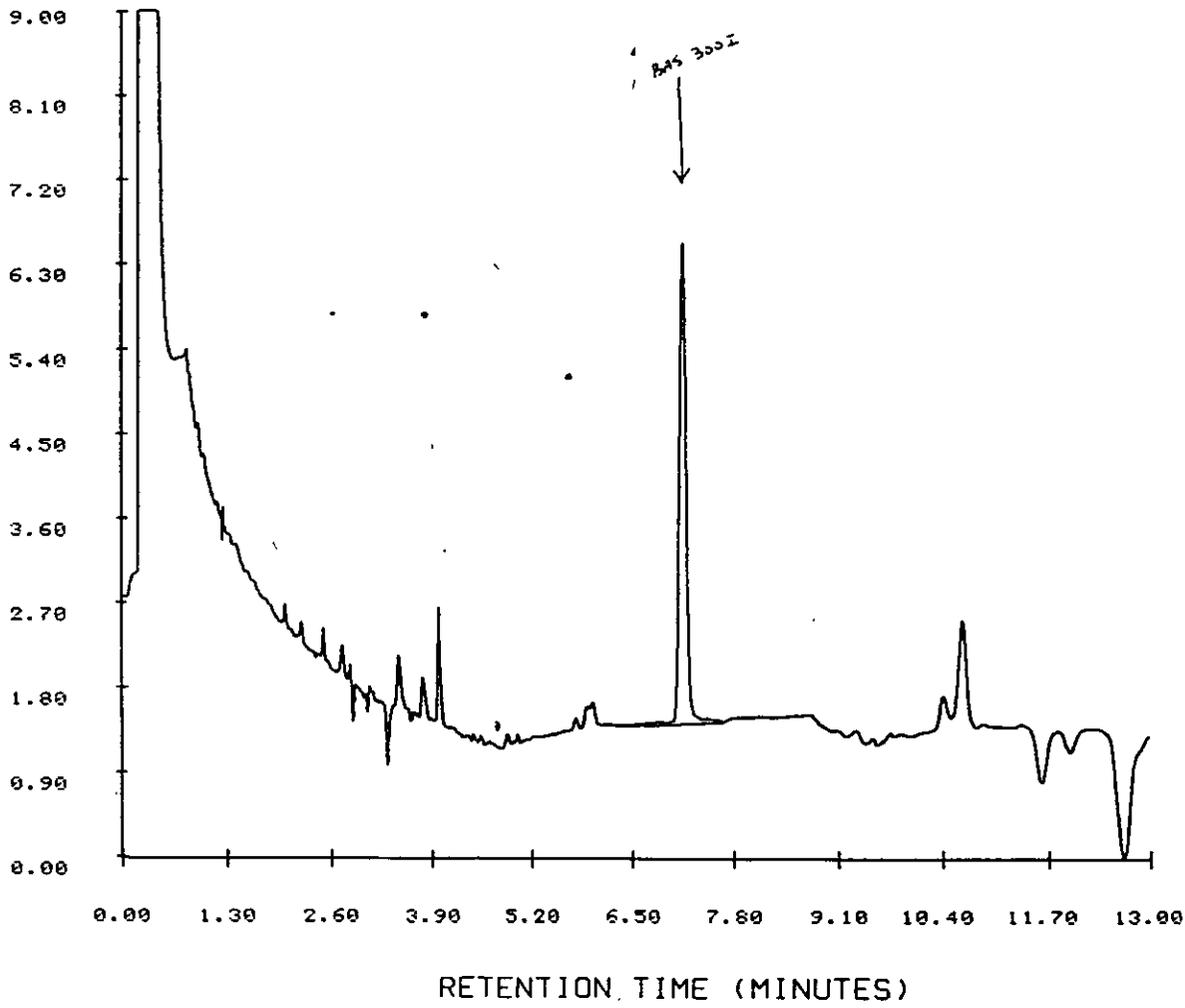
TEST NO.: B3001

DATE TIME: 07/19/93 07:12:58

METHOD NO.: B3001 / B3001

PAGE NO.: 01

1401.532



Y MAXIMUM: 54433.

START TIME: 0.00

Y MINIMUM: 52783.

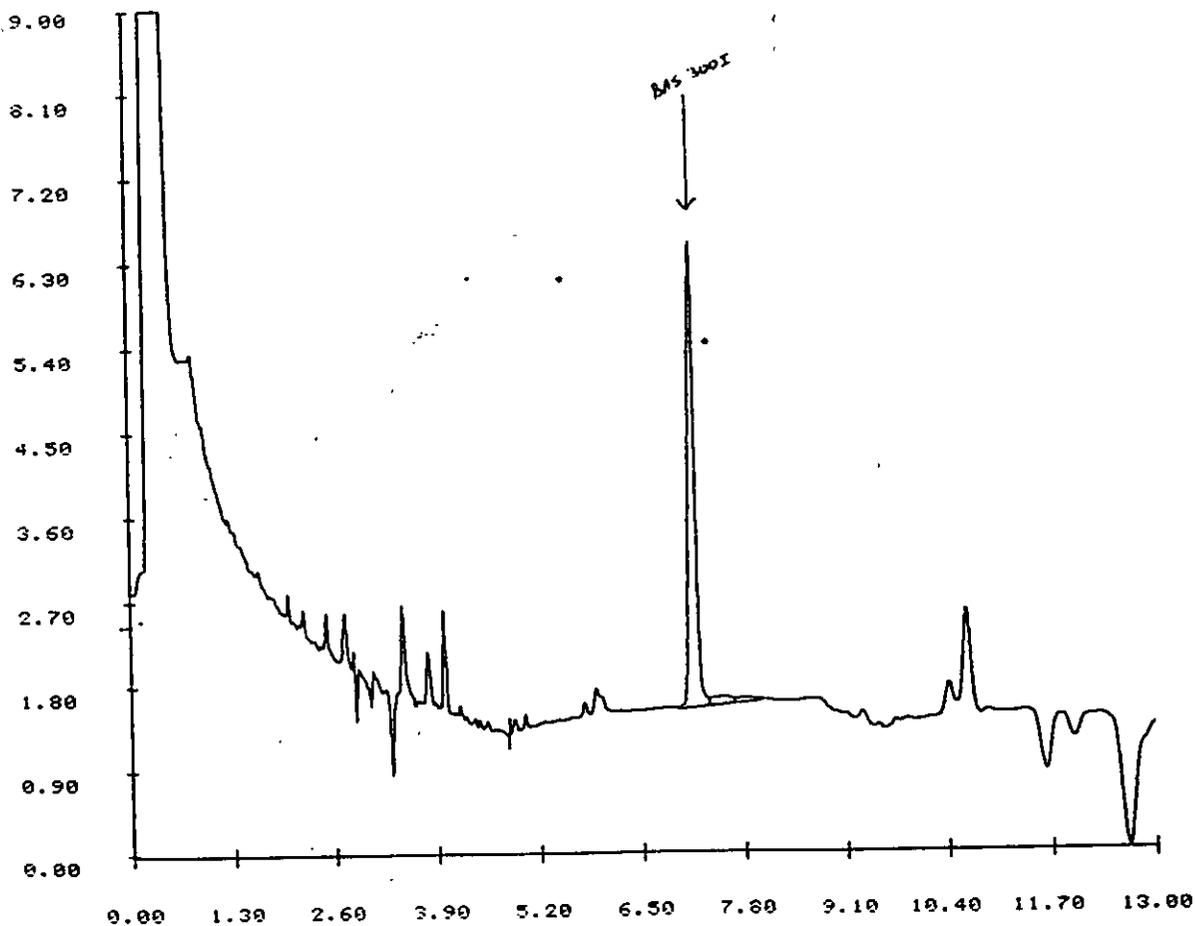
END TIME: 13.00

Figure 11. Chromatogram of a control whole orange sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-1, Sample Number 109279. See Table III.

### 0.50 PPM B ORANGE

SAMPLE NO.: 109279 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 07/19/93 08:03:20  
PAGE NO.: 01



RETENTION TIME (MINUTES)

γ MAXIMUM: 54460.  
γ MINIMUM: 52751.

START TIME: 0.00  
END TIME: 13.00

Figure 12.

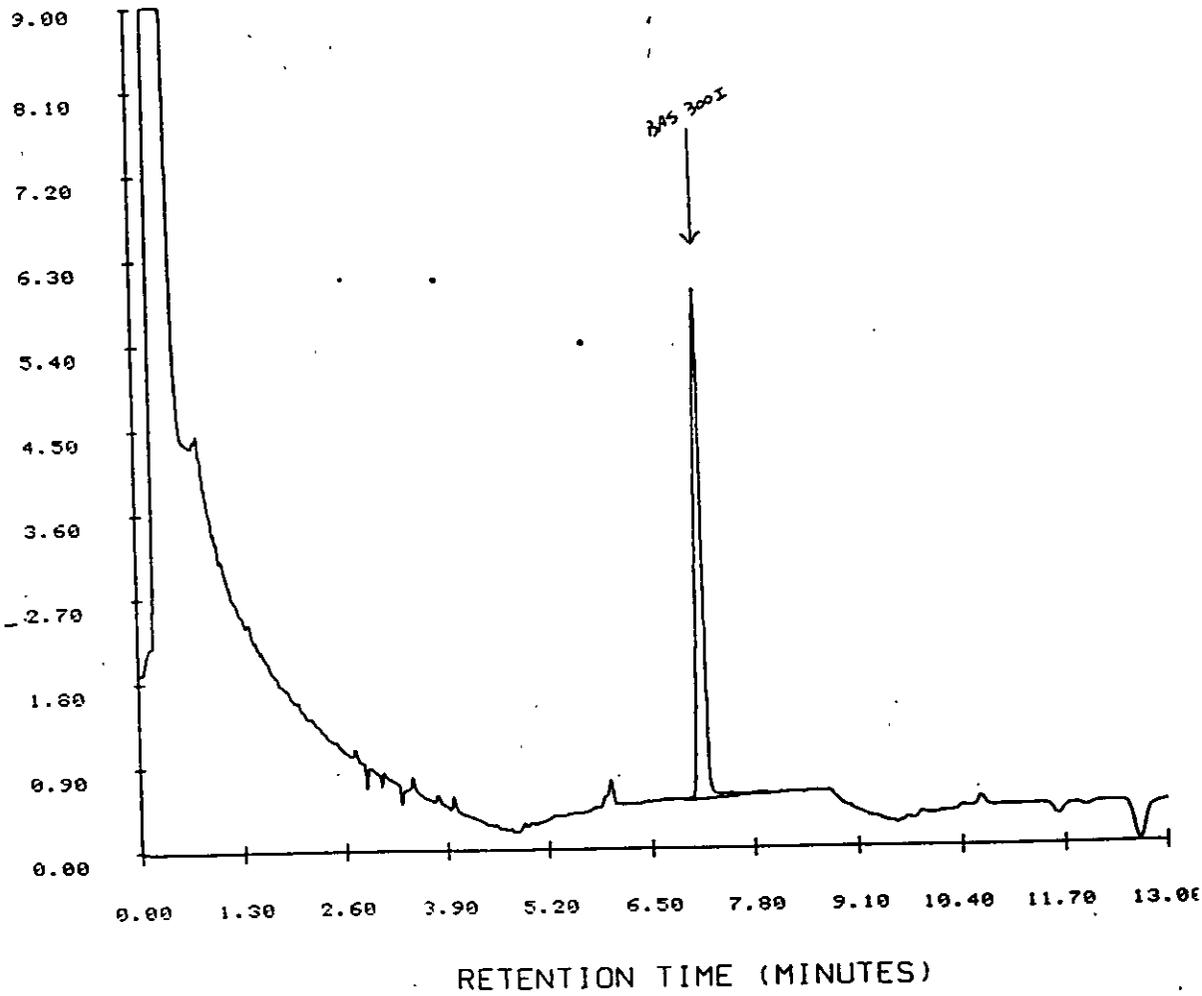
Chromatogram of a control whole orange sample fortified with 5.0 ppm of BAS 300 I. Master Sheet 93102-1, Sample Number 109281. See Table III.

### 5.0 PPM A ORANGE

SAMPLE NO.: 109281 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 07/19/93 09:27:12  
PAGE NO.: 01

9483.758



Y MAXIMUM: 54523.  
Y MINIMUM: 52937.

START TIME: 0.00  
END TIME: 13.00

UP # UNOUR UNITIC

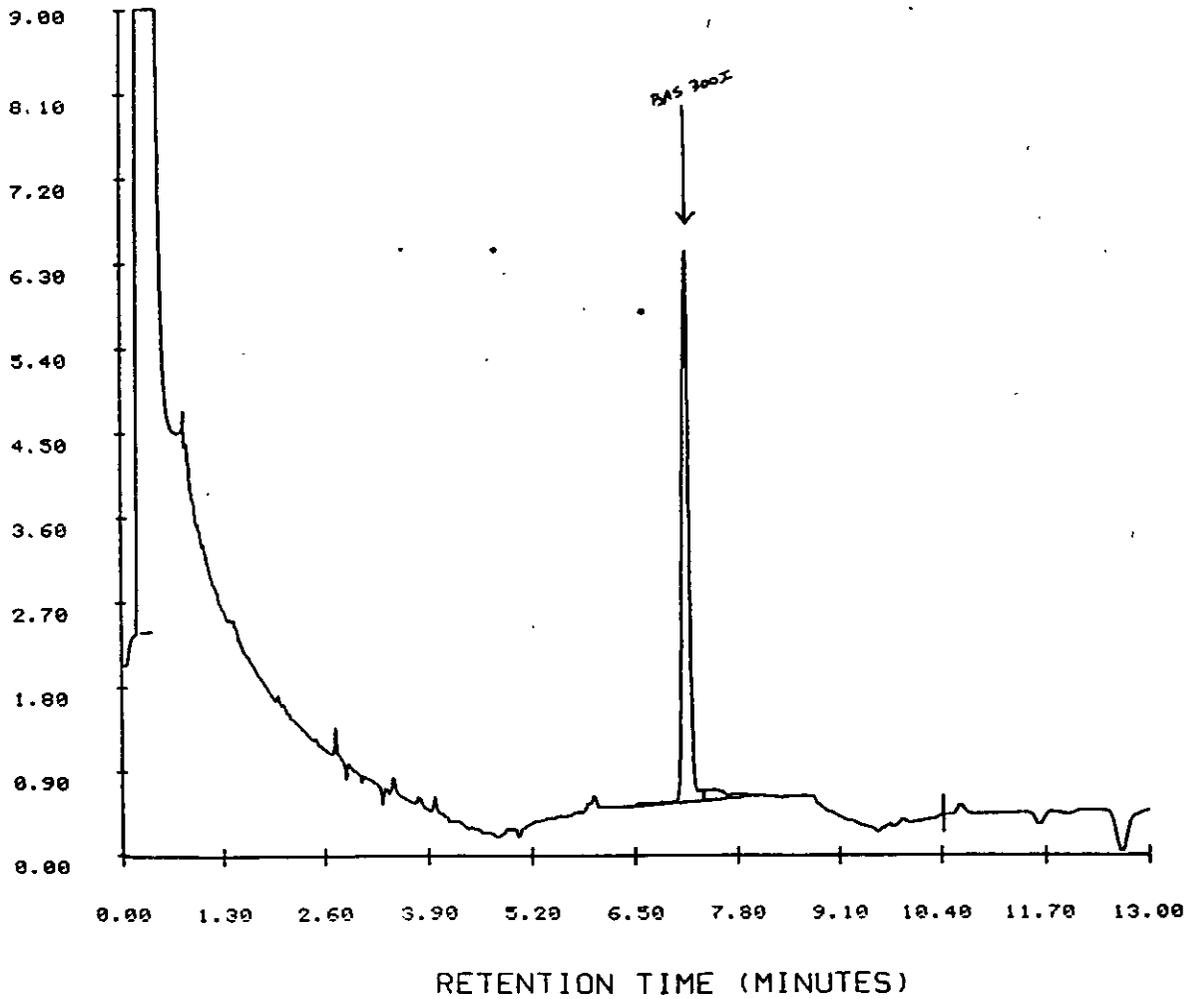
Figure 13.

Chromatogram of a control whole orange sample fortified with 5.0 ppm of BAS 300 I. Master Sheet 93102-1, Sample Number 109282. See Table III.

### 5.0 PPM C ORANGE

SAMPLE NO.: 109283 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 07/19/93 10:51:05  
PAGE NO.: 01

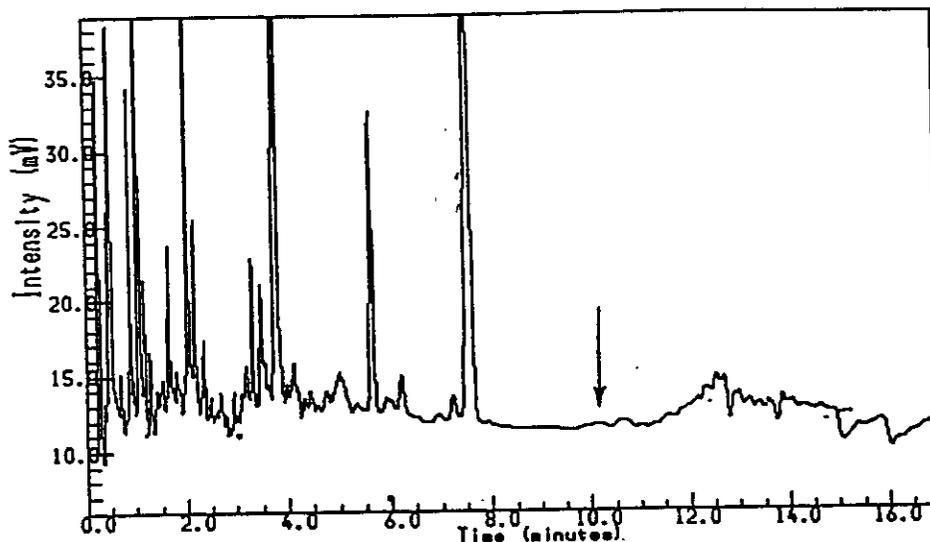


Y MAXIMUM: 54407.  
Y MINIMUM: 52942.

START TIME: 0.00  
END TIME: 13.00

Figure 14. Chromatogram of a control whole orange sample. (Analyzed by the alternative procedure.) Master Sheet 93102-24, Sample Number 3. See Table IV.

Acquired on 8-OCT-1993 at 09:52



BASF CORP. - VAX MULTICHROM

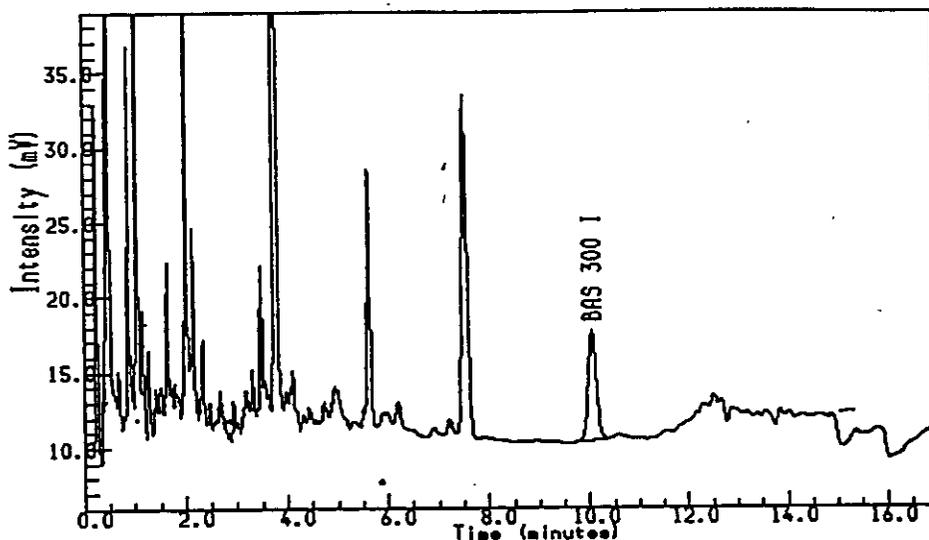
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : CONTROL ORANGE  
 Sample Id : 9390101  
 Sample Type : Control Amount=1.00000  
 Bottle No : 3

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
<u>Totals</u>			
Unknowns	0	N/A	
	0	0.000	
	0	0.000	

Figure 15. Chromatogram of a control whole orange sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. (Analyzed by the alternative procedure.) Master Sheet 93102-24, Sample Number 8. See Table IV.

Acquired on 8-OCT-1993 at 11:39



BASF CORP. - VAX MULTICHROM

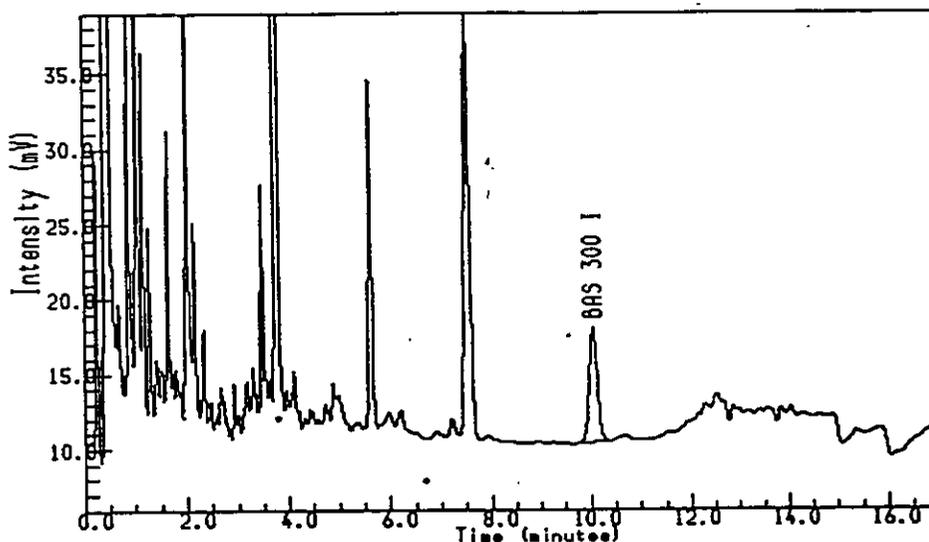
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.05PPM A  
 Sample Id : 9390101  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 8

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.059	7313	39.317	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	7313	39.317	
	7313	39.317	

Figure 16. Chromatogram of a control whole orange sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. (Analyzed by the alternative procedure.) Master Sheet 93102-24, Sample Number 10. See Table IV.

Acquired on 8-OCT-1993 at 12:23



BASF CORP. - VAX MULTICHROM

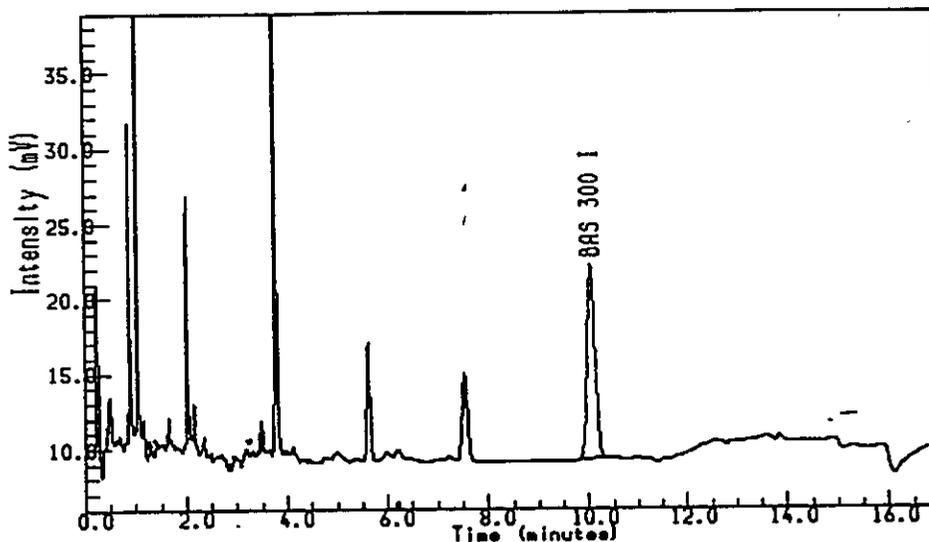
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.05PPM B  
 Sample Id : 9390101  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 10

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.064	7655	41.458	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	7655	41.458	
	7655	41.458	

Figure 17. Chromatogram of a control whole orange sample fortified with 0.50 ppm of BAS 300 I. (Analyzed by the alternative procedure.) Master Sheet 93102-24, Sample Number 15. See Table IV.

Acquired on 8-OCT-1993 at 14:11



BASF CORP. - VAX MULTICHROM

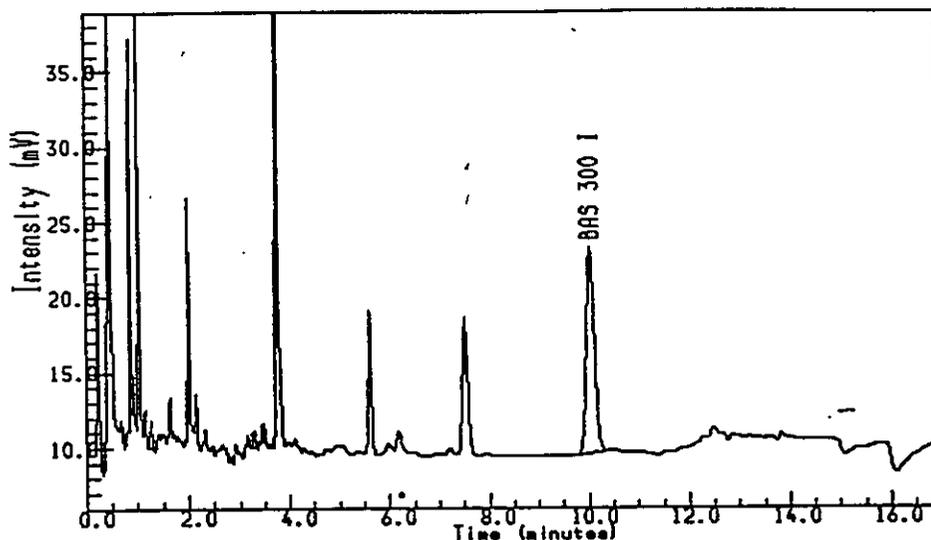
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.5PPM A  
 Sample Id : 9390101  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 14

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.075	13005	383.403	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	13005	383.403	
	13005	383.403	

Figure 18. Chromatogram of a control whole orange sample fortified with 0.50 ppm of BAS 300 I. (Analyzed by the alternative procedure.) Master Sheet 93102-24, Sample Number 18. See Table IV.

Acquired on 8-OCT-1993 at 15:16



BASF CORP. - VAX MULTICHROM

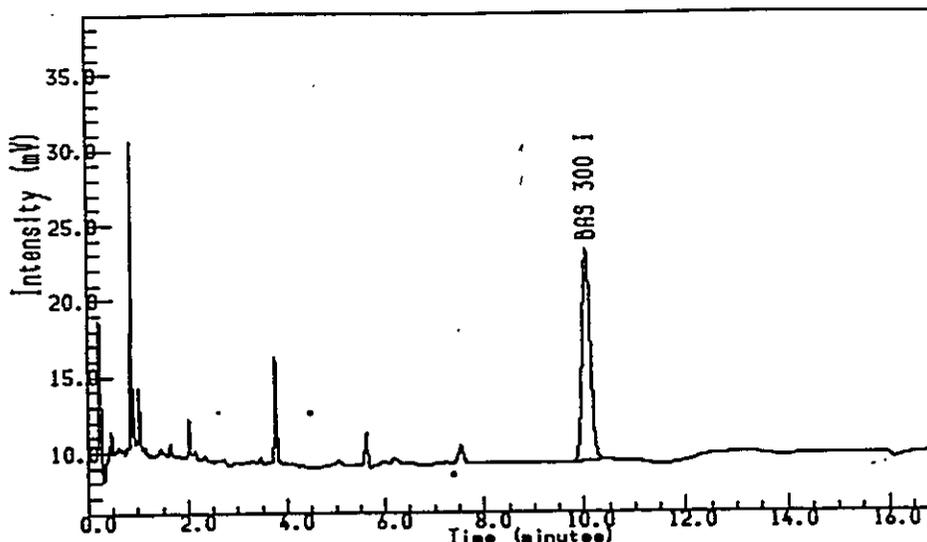
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.50PPM B  
 Sample Id : 9390101  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 17

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.059	13658	405.807	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	13658	405.807	
	13658	405.807	

Figure 19. Chromatogram of a control whole orange sample fortified with 5.0 ppm of BAS 300 I. (Analyzed by the alternative procedure.) Master Sheet 93102-24, Sample Number 22. See Table IV.

Acquired on 8-OCT-1993 at 16:42



BASF CORP. - VAX MULTICHROM

Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 5.0PPM A  
 Sample Id : 9390101  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 21

PEAK INFORMATION

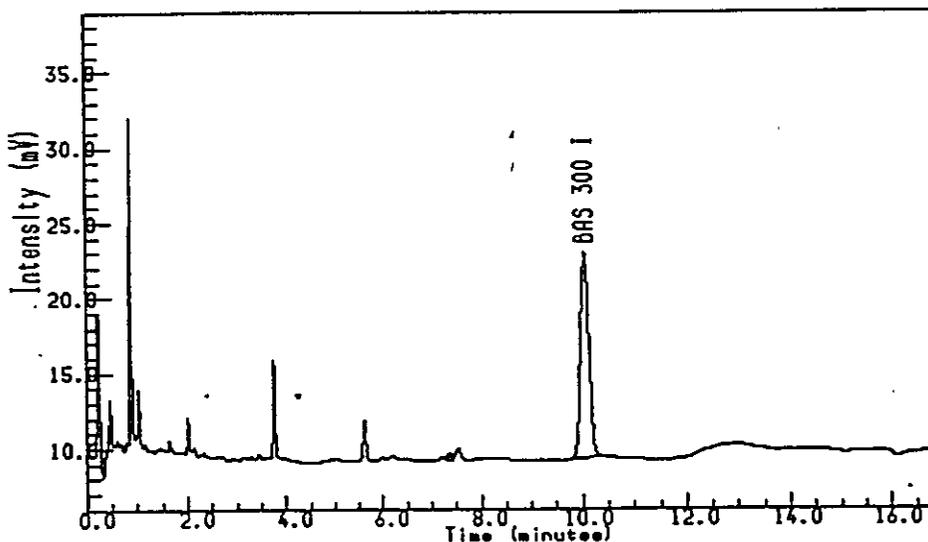
RT mins	Hght uV	ppb	Peak name
10.064	14005	4177.904	BAS 300 I

Totals

Unknowns	0	N/A
	14005	4177.904
	14005	4177.904

Figure 20. Chromatogram of a control whole orange sample fortified with 5.0 ppm of BAS 300 I. (Analyzed by the alternative procedure.) Master Sheet 93102-24, Sample Number 23. See Table IV.

Acquired on 8-OCT-1993 at 17:03



BASF CORP. - VAX MULTICHROM

Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 5.0PPM B  
 Sample Id : 9390101  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 22

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.059	13744	4087.972	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	13744	4087.972	
	13744	4087.972	

Figure 21. Chromatogram of a control orange peel sample. Master Sheet 93102-10, Sample Number 110022. See Table V.

PERKIN-ELMER CORP PART NO. N625-1026

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PERKIN-ELM

### CONTROL

SAMPLE NO.: 110022 .01

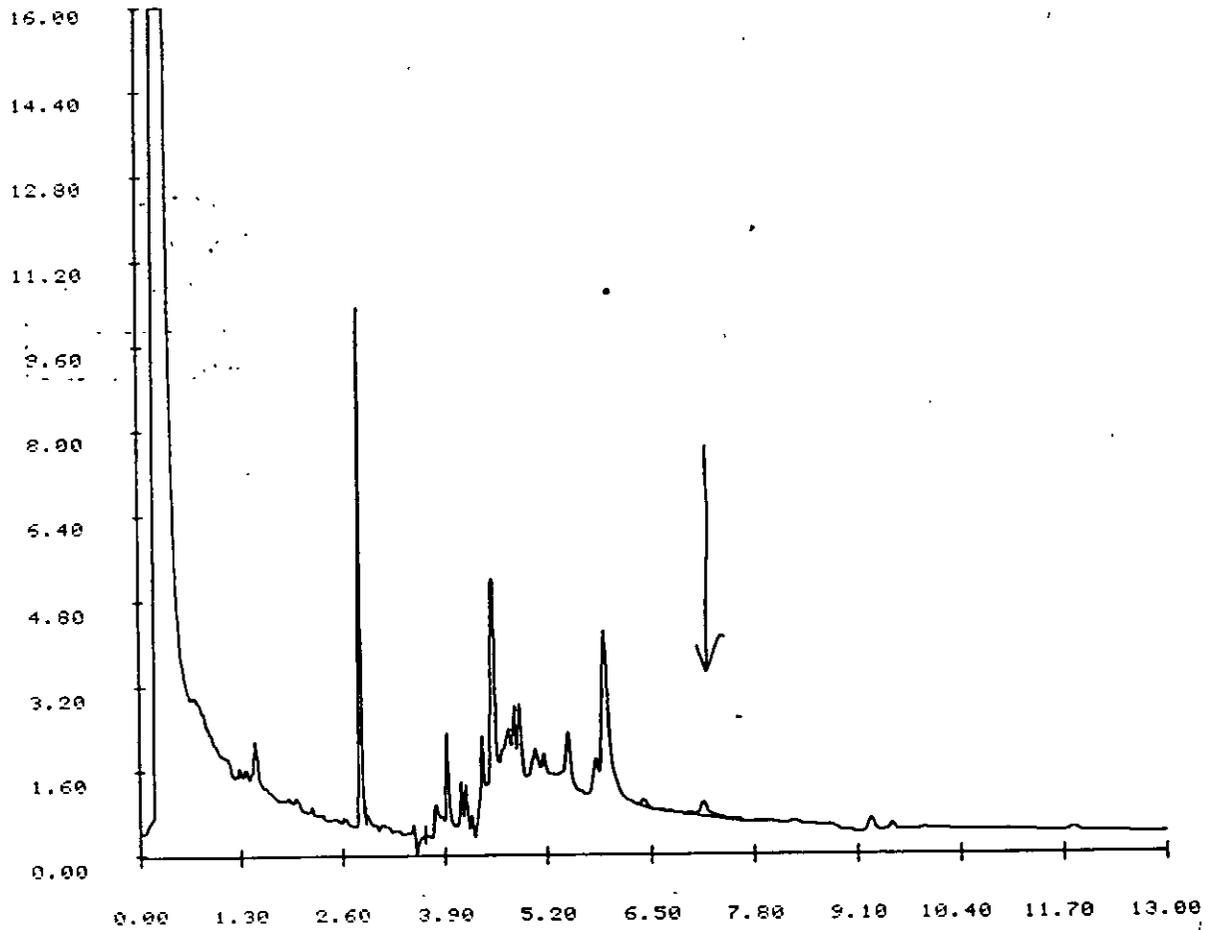
INSTRUMENT: 19

TEST NO.: B3001

DATE TIME: 08/19/93 20:12:49

METHOD NO.: B3001 / B3001

PAGE NO.: 01



RETENTION TIME (MINUTES)

Y MAXIMUM: 55141.

START TIME: 0.00

Y MINIMUM: 52163.

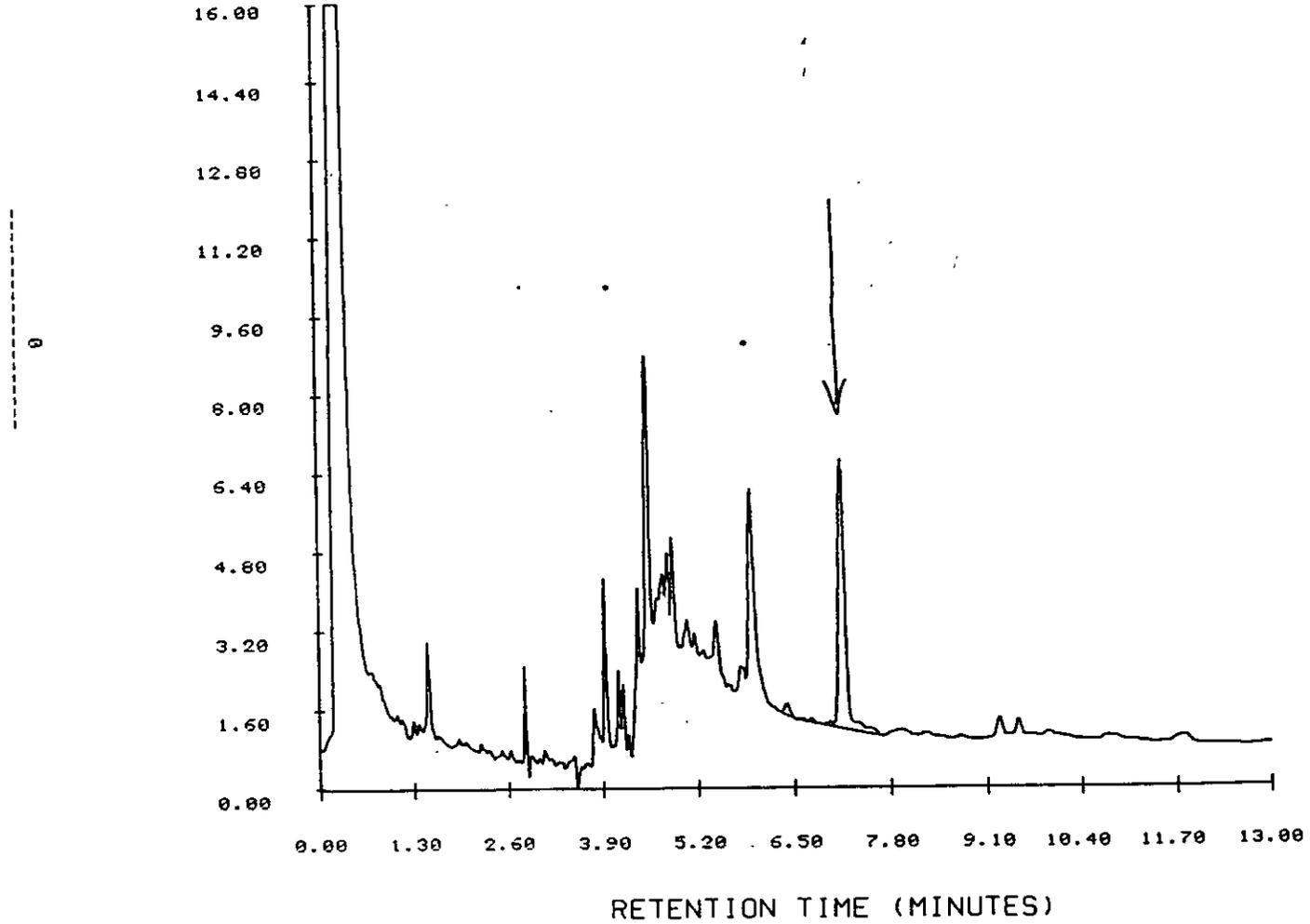
END TIME: 13.00

Figure 22. Chromatogram of a control orange peel sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-10, Sample Number 110024. See Table V.

0.05PPM FORT

SAMPLE NO.: 110024 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 08/19/93 21:42:27  
PAGE NO.: 01



Y MAXIMUM: 54238.  
Y MINIMUM: 52115.

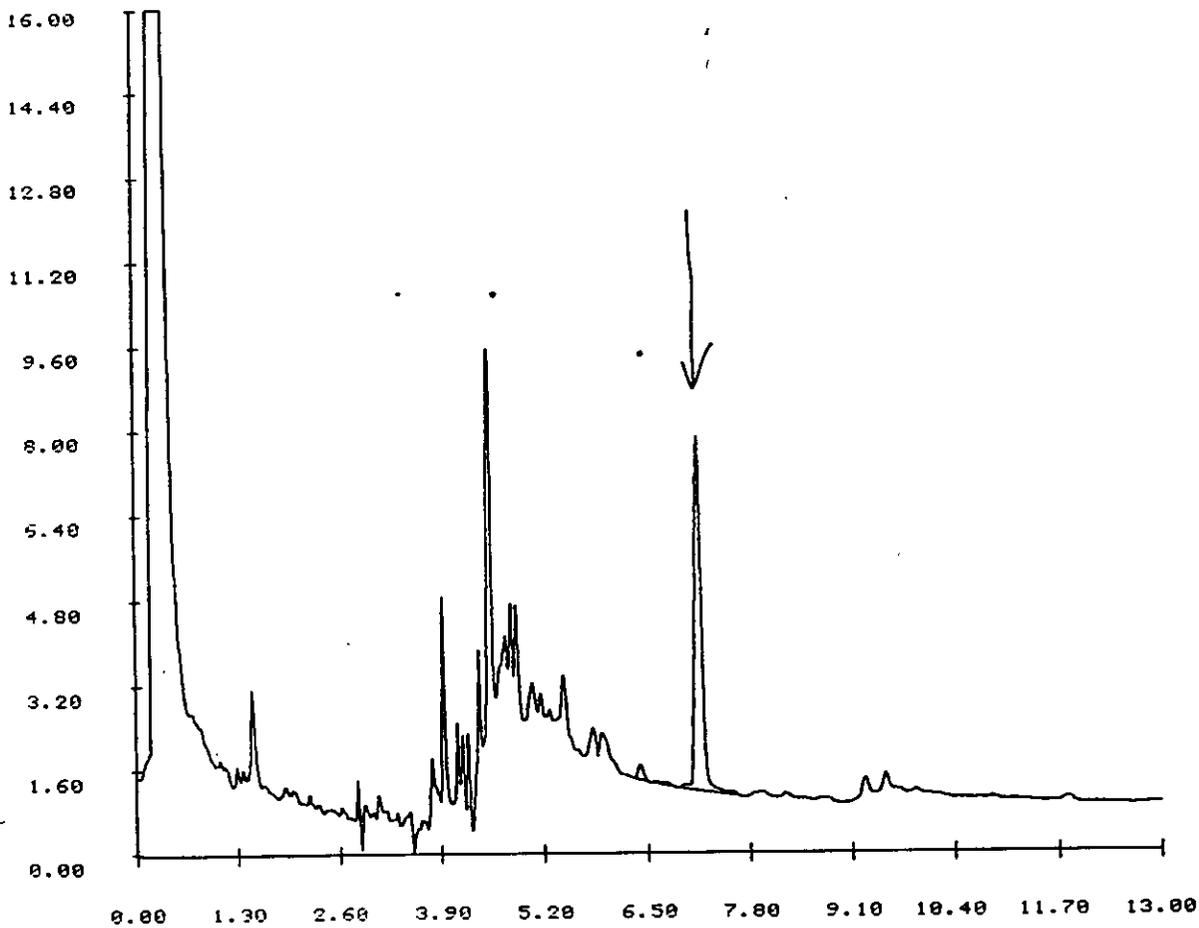
START TIME: 0.00  
END TIME: 13.00

Figure 23. Chromatogram of a control orange peel sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-10, Sample Number 110025. See Table V.

0.05PPM

SAMPLE NO.: 110025 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 08/19/93 22:18:04  
PAGE NO.: 01



RETENTION TIME (MINUTES)

Y MAXIMUM: 53789.

START TIME: 0.00

Y MINIMUM: 52137.

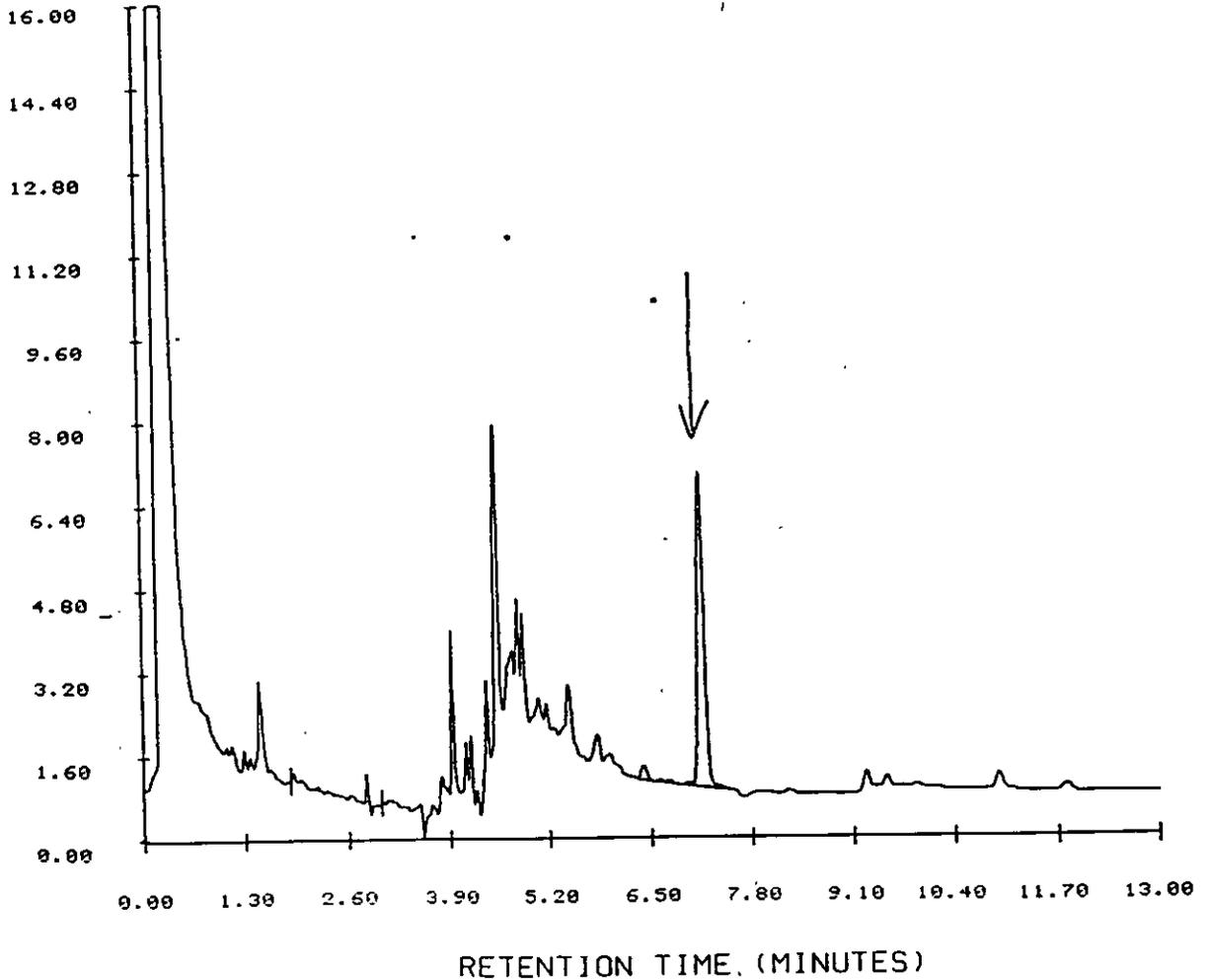
END TIME: 13.00

Figure 24. Chromatogram of a control orange peel sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-10, Sample Number 110026. See Table V.

### 0.05PPM.FORT

SAMPLE NO.: 110026 .01  
TEST NO.: B300I  
METHOD NO.: B300I / B300I

INSTRUMENT: 19  
DATE TIME: 08/19/93 22:53:41  
PAGE NO.: 01



Y MAXIMUM: 54011.  
Y MINIMUM: 52122.

START TIME: 0.00  
END TIME: 13.00

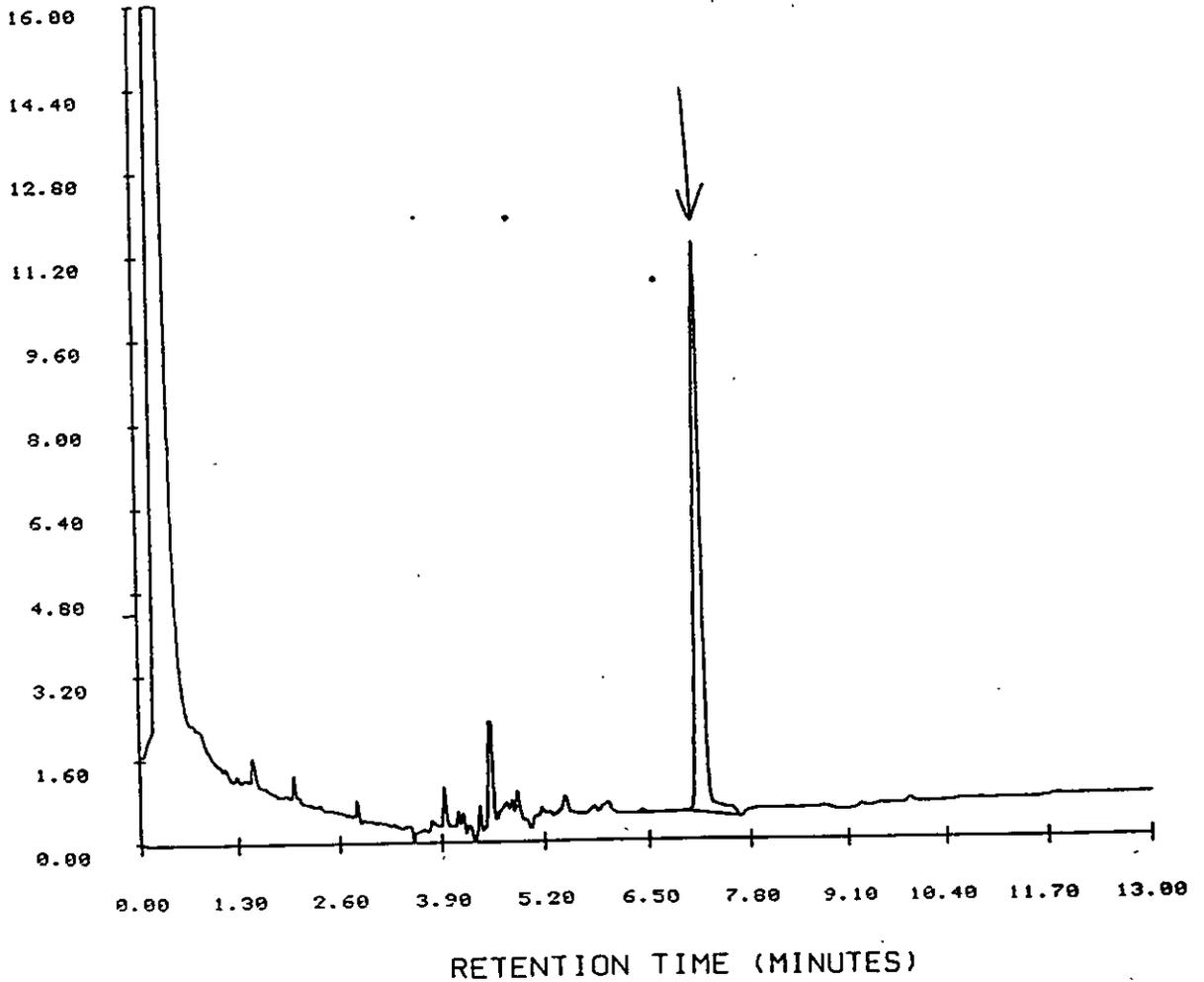
Figure 25.

Chromatogram of a control orange peel sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-10, Sample Number 110027. See Table V.

0.5PPM

SAMPLE NO.: 110027 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 08/19/93 23:29:15  
PAGE NO.: 01



Y MAXIMUM: 53763.  
Y MINIMUM: 52108.

START TIME: 0.00  
END TIME: 13.00

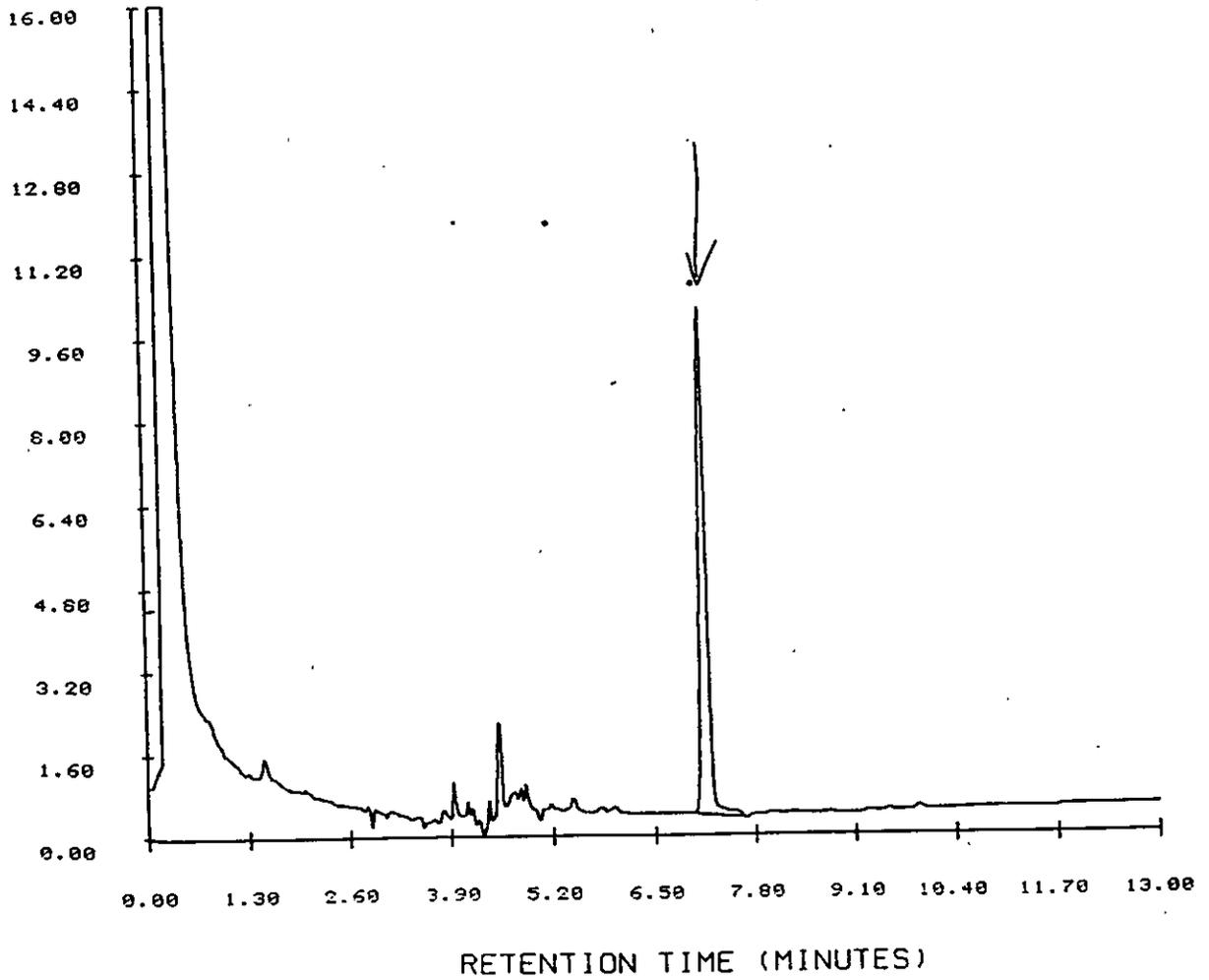
Figure 26.

Chromatogram of a control orange peel sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-10, Sample Number 110028. See Table V.

### 0.5PPM

SAMPLE NO.: 110028 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 08/20/93 00:22:40  
PAGE NO.: 01



Y MAXIMUM: 54051.  
Y MINIMUM: 52109.

START TIME: 0.00  
END TIME: 13.00

Figure 27.

Chromatogram of a control orange peel sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-10, Sample Number 110029. See Table V.

0.5PPM

SAMPLE NO.: 110029 .01

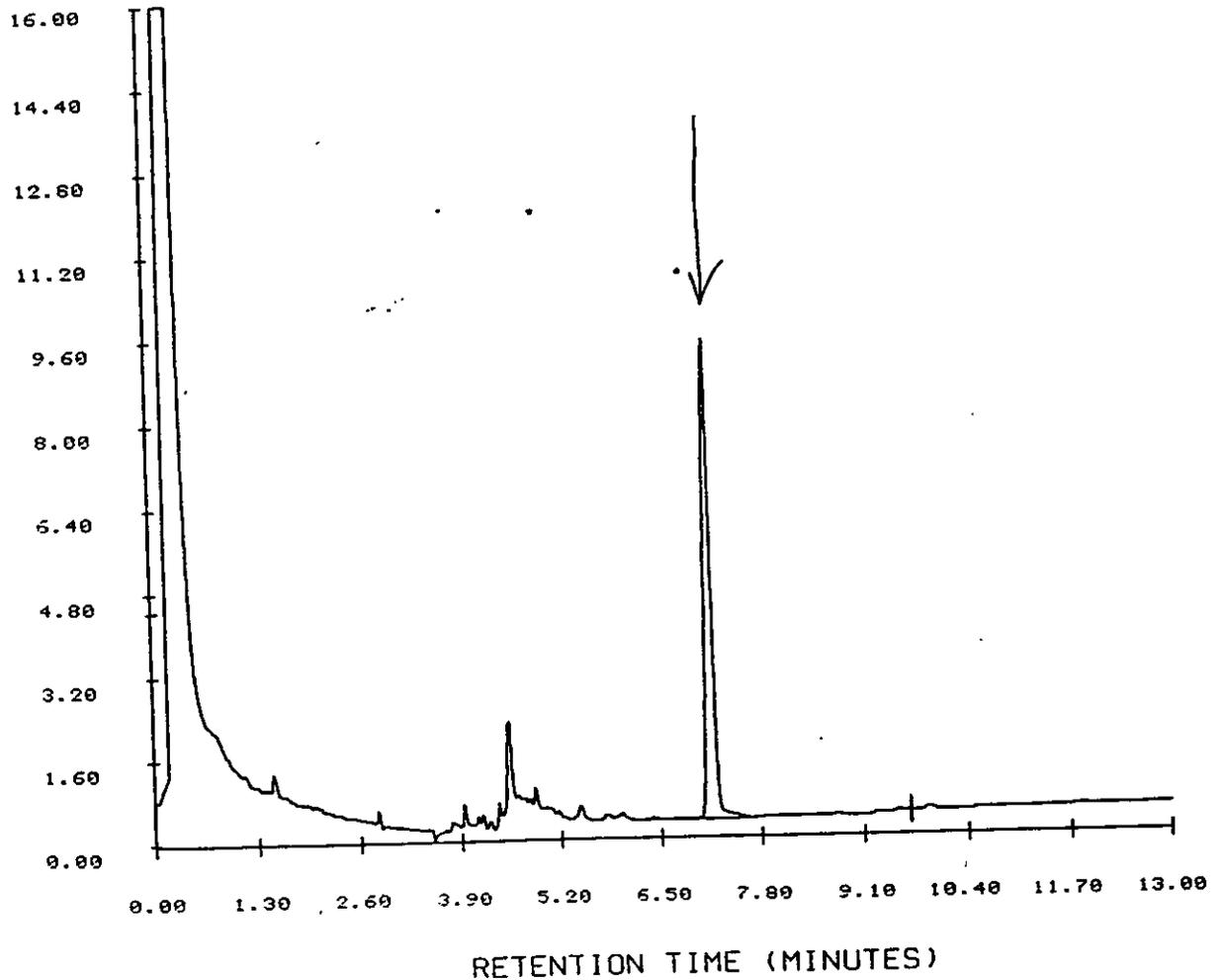
INSTRUMENT: 19

TEST NO.: B3001

DATE TIME: 08/20/93 00:40:27

METHOD NO.: B3001 / B3001

PAGE NO.: 01



Y MAXIMUM: 54146.

START TIME: 0.00

Y MINIMUM: 52113.

END TIME: 13.00

Figure 28.

Chromatogram of a control orange peel sample fortified with 5.0 ppm of BAS 300 I. Master Sheet 93102-10, Sample Number 110030. See Table V.

5.00PPM

SAMPLE NO.: 110030 .01

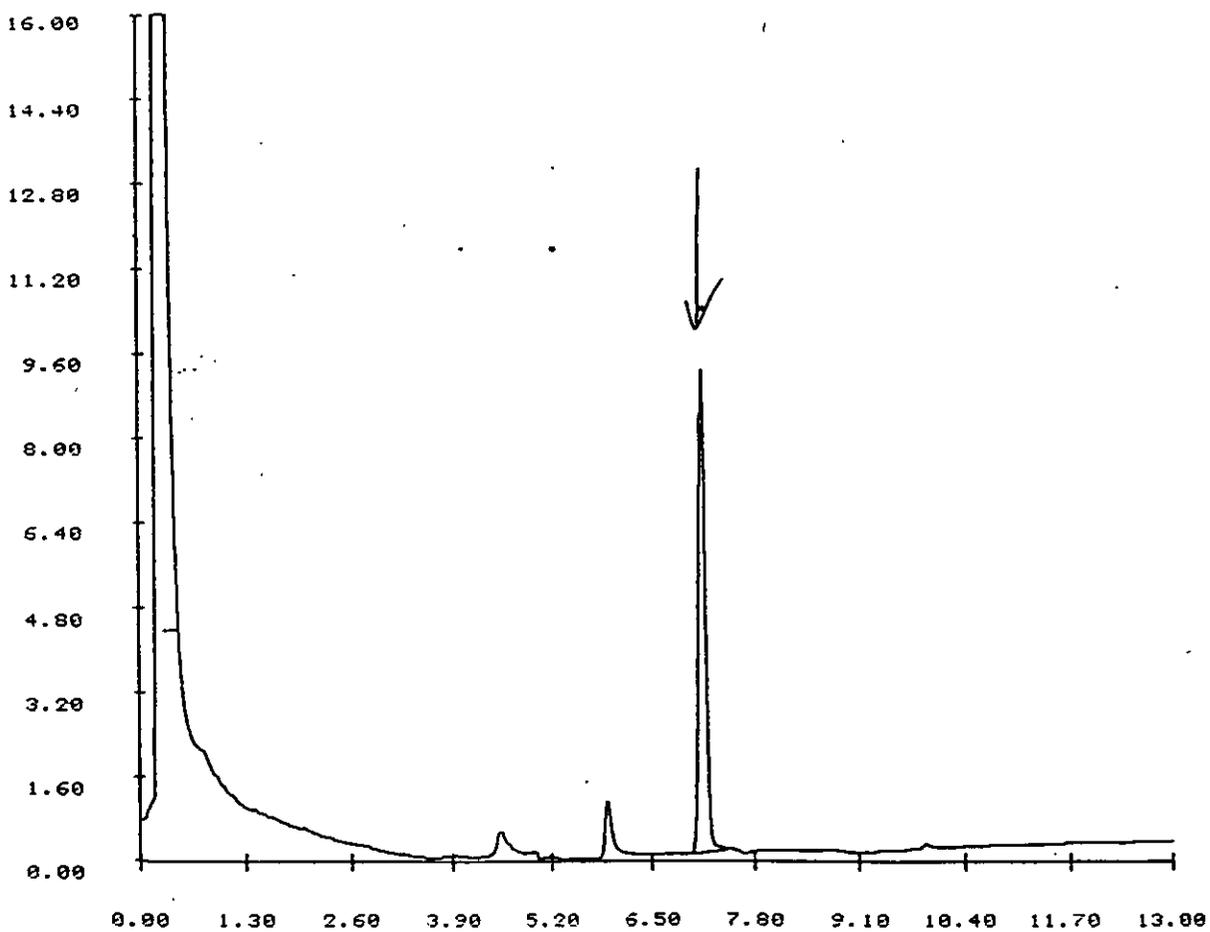
INSTRUMENT: 19

TEST NO.: B3001

DATE TIME: 06/20/93 01:33:50

METHOD NO.: B3001 / B3001

PAGE NO.: 01



RETENTION TIME (MINUTES)

Y MAXIMUM: 54182.

START TIME: 0.00

Y MINIMUM: 52116.

END TIME: 13.00

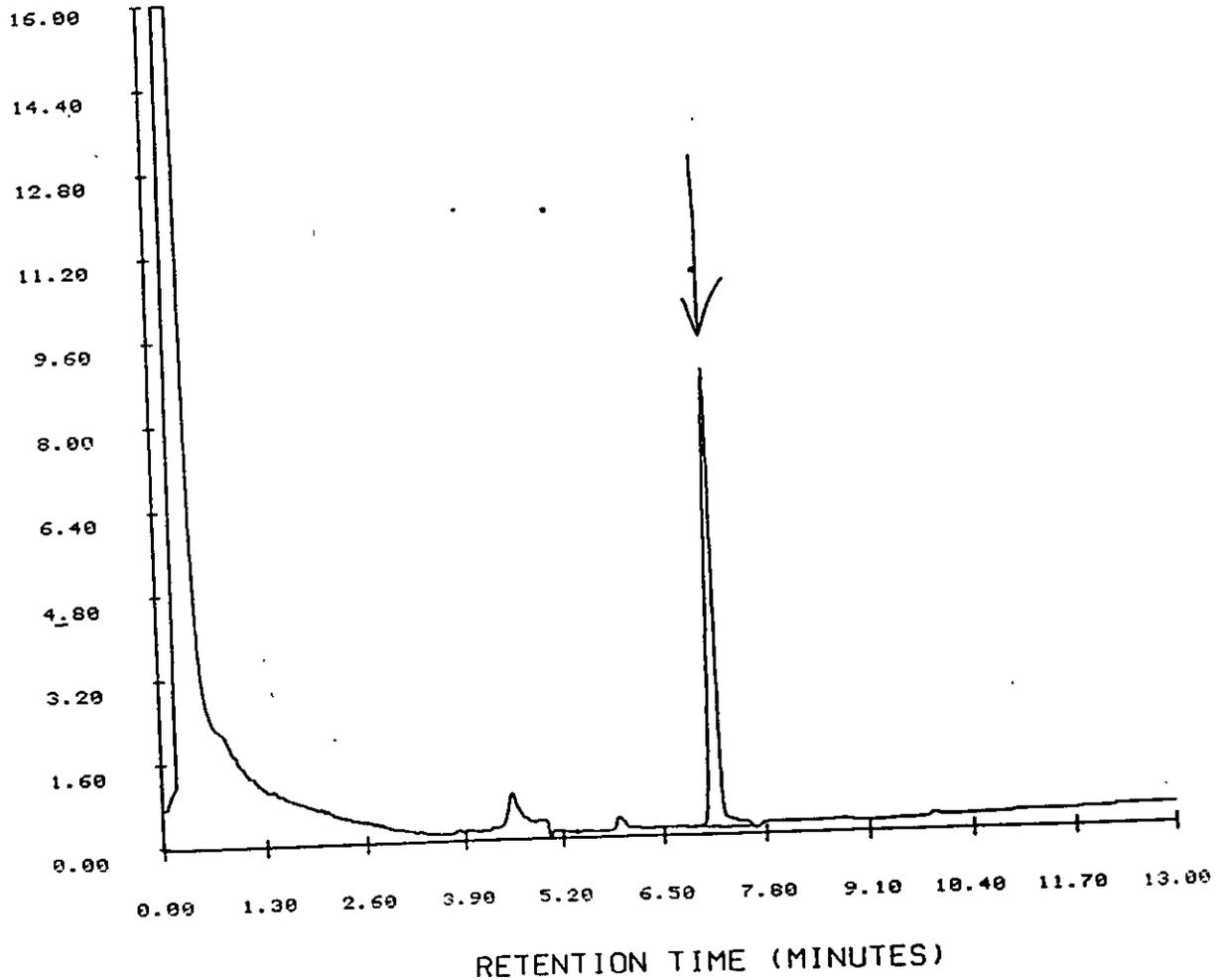
Figure 29.

Chromatogram of a control orange peel sample fortified with 5.0 ppm of BAS 300 I. Master Sheet 93102-10, Sample Number 110031. See Table V.

5.0PPM

SAMPLE NO.: 110031 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 08/20/93 01:51:39  
PAGE NO.: 01



Y MAXIMUM: 54263.  
Y MINIMUM: 52117.

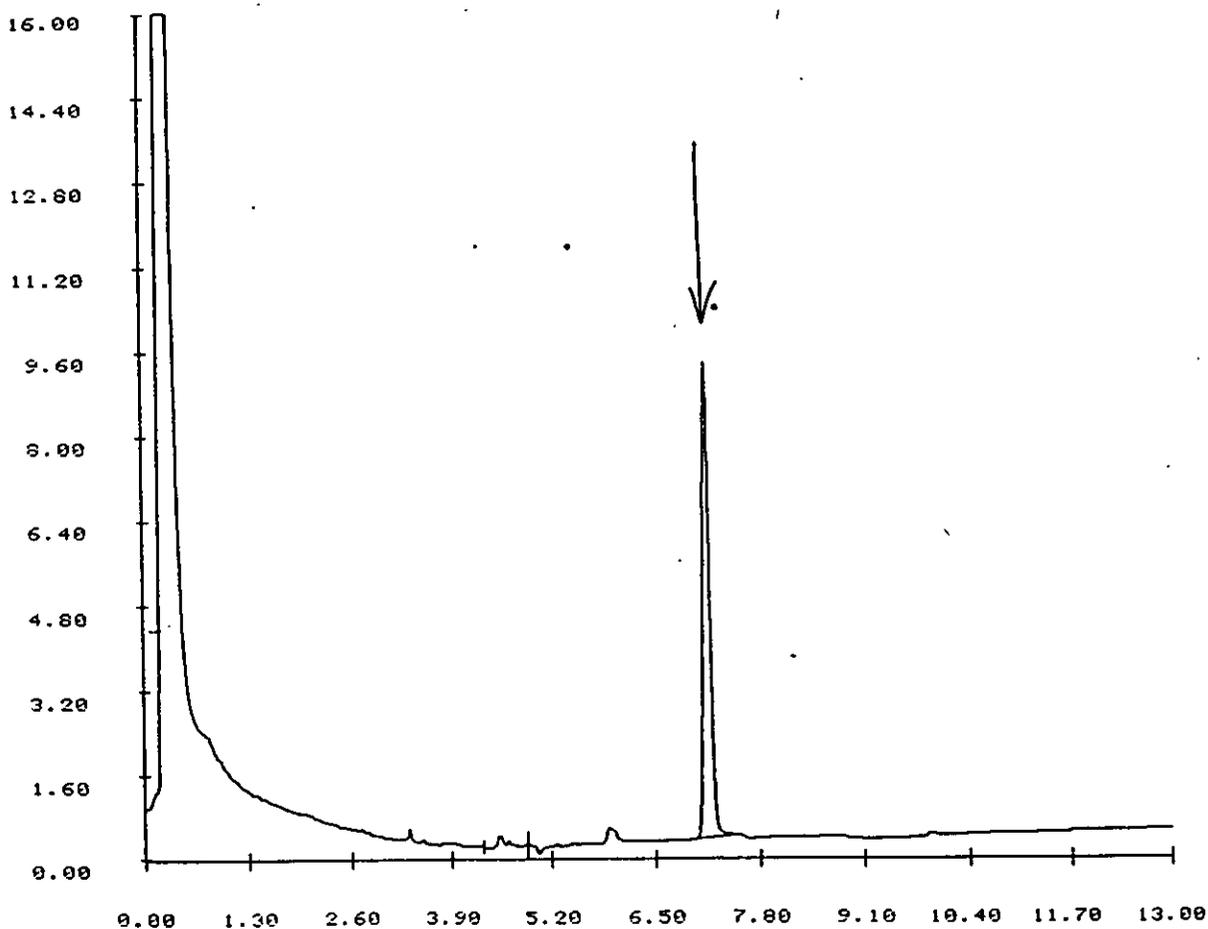
START TIME: 0.00  
END TIME: 13.00

Figure 30. Chromatogram of a control orange peel sample fortified with 5.0 ppm of BAS 300 I. Master Sheet 93102-10, Sample Number 110032. See Table V.

### 5.00PPM

SAMPLE NO.: 110032 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 08/20/93 02:44:59  
PAGE NO.: 01



RETENTION TIME (MINUTES)

Y MAXIMUM: 54225.  
Y MINIMUM: 52087.

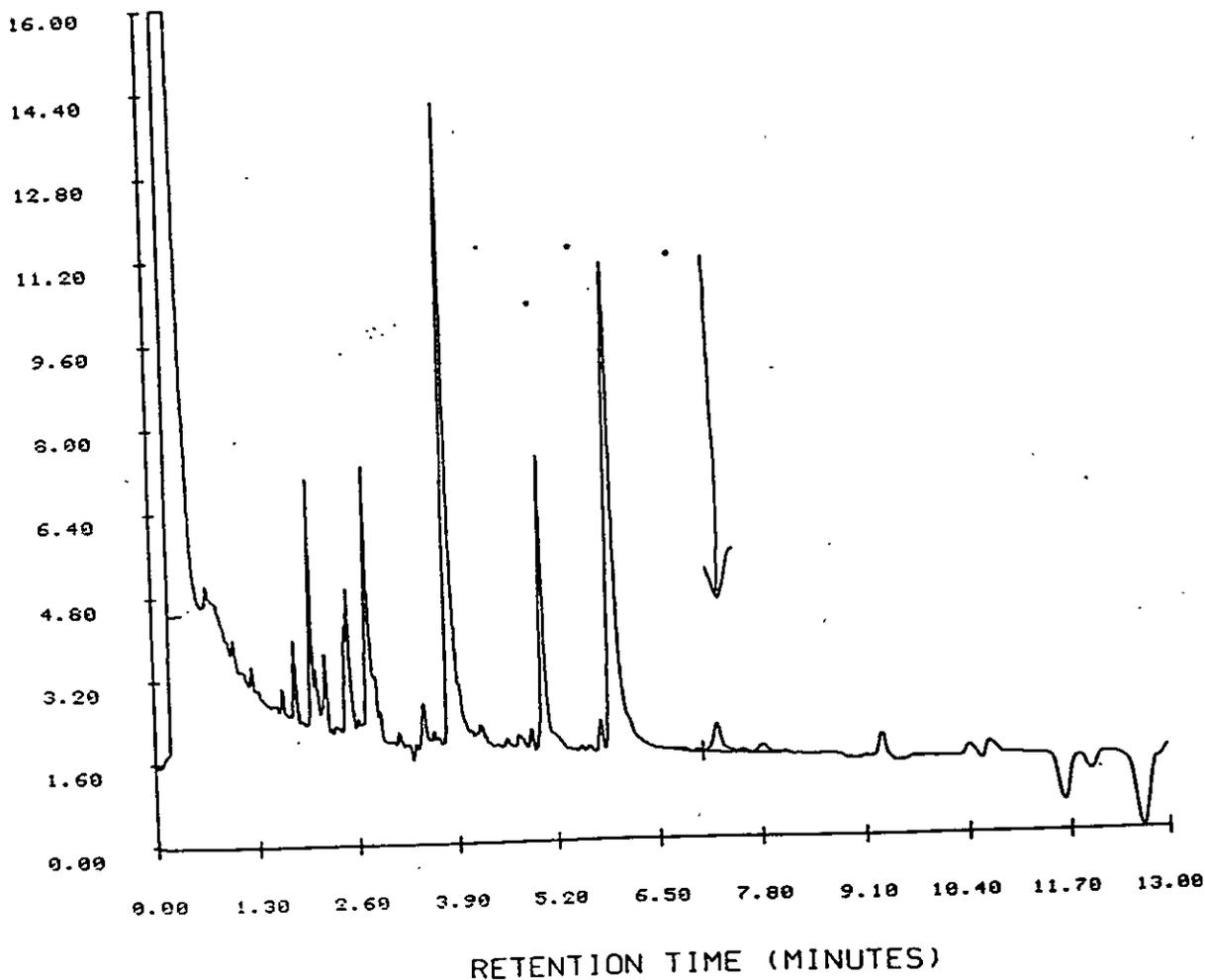
START TIME: 0.00  
END TIME: 13.00

Figure 31. Chromatogram of a control orange juice sample. Master Sheet 93102-11, Sample Number 110175. See Table VI.

### CONTROL JUICE

SAMPLE NO.: 110175 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 08/24/93 20:09:53  
PAGE NO.: 01



Y MAXIMUM: 54663.  
Y MINIMUM: 51827.

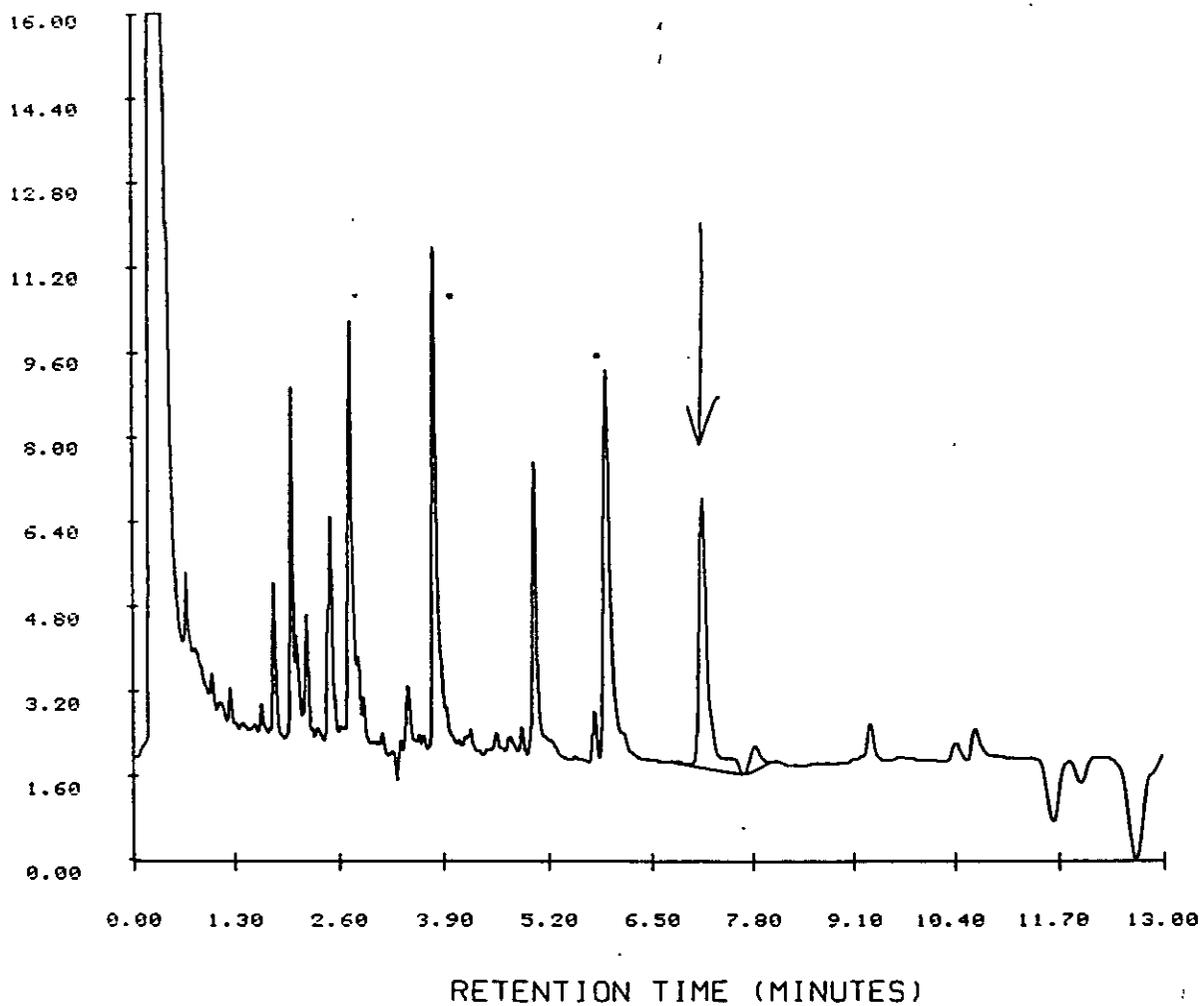
START TIME: 0.00  
END TIME: 13.00

Figure 32. Chromatogram of a control orange juice sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-11, Sample Number 110177. See Table VI.

0.05PPM.

SAMPLE NO.: 110177 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 08/24/93 21:09:57  
PAGE NO.: 01



Y MAXIMUM: 53898.  
Y MINIMUM: 51794.

START TIME: 0.00  
END TIME: 13.00

Figure 33.

Chromatogram of a control orange juice sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-11, Sample Number 110178. See Table VI.

0.05PPM

SAMPLE NO.: 110178 .01

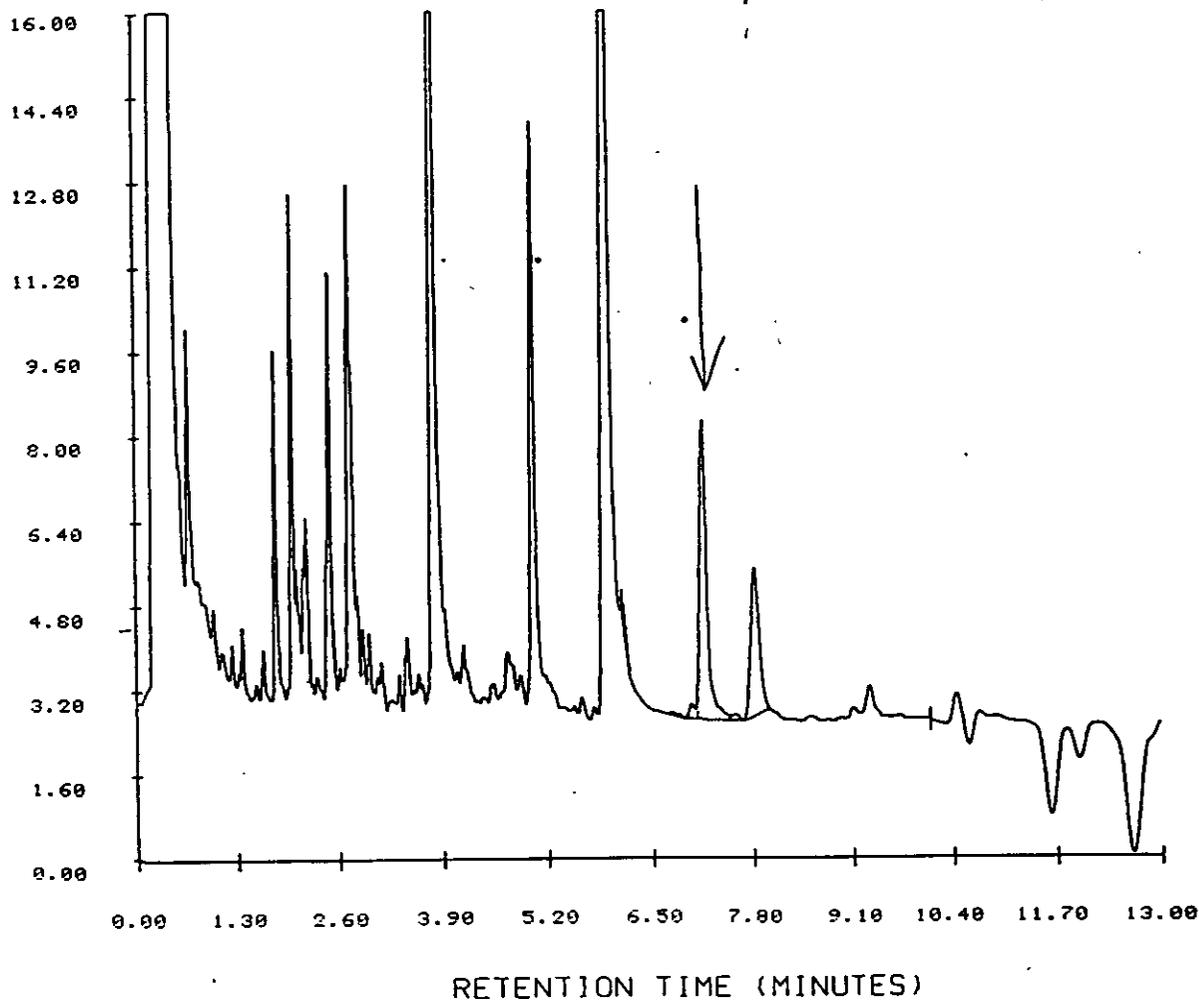
INSTRUMENT: 19

TEST NO.: B3001

DATE TIME: 08/24/93 21:48:39

METHOD NO.: B3001 / B3001

PAGE NO.: 01



Y MAXIMUM: 53612.

START TIME: 0.00

Y MINIMUM: 51759.

END TIME: 13.00

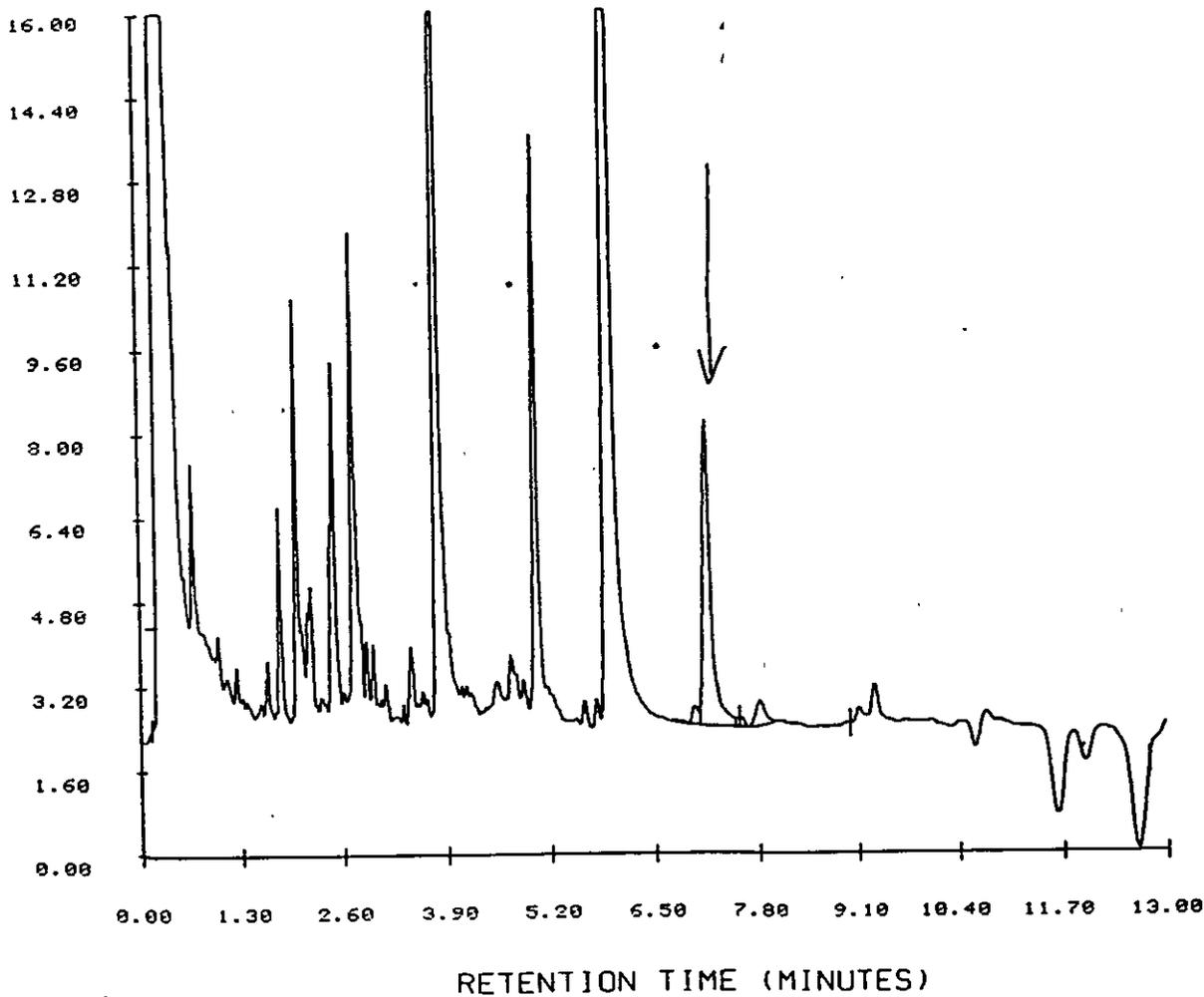
Figure 34.

Chromatogram of a control orange juice sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-11, Sample Number 110179. See Table VI.

0.05PPM

SAMPLE NO.: 110179 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 08/24/93 22:25:53  
PAGE NO.: 01



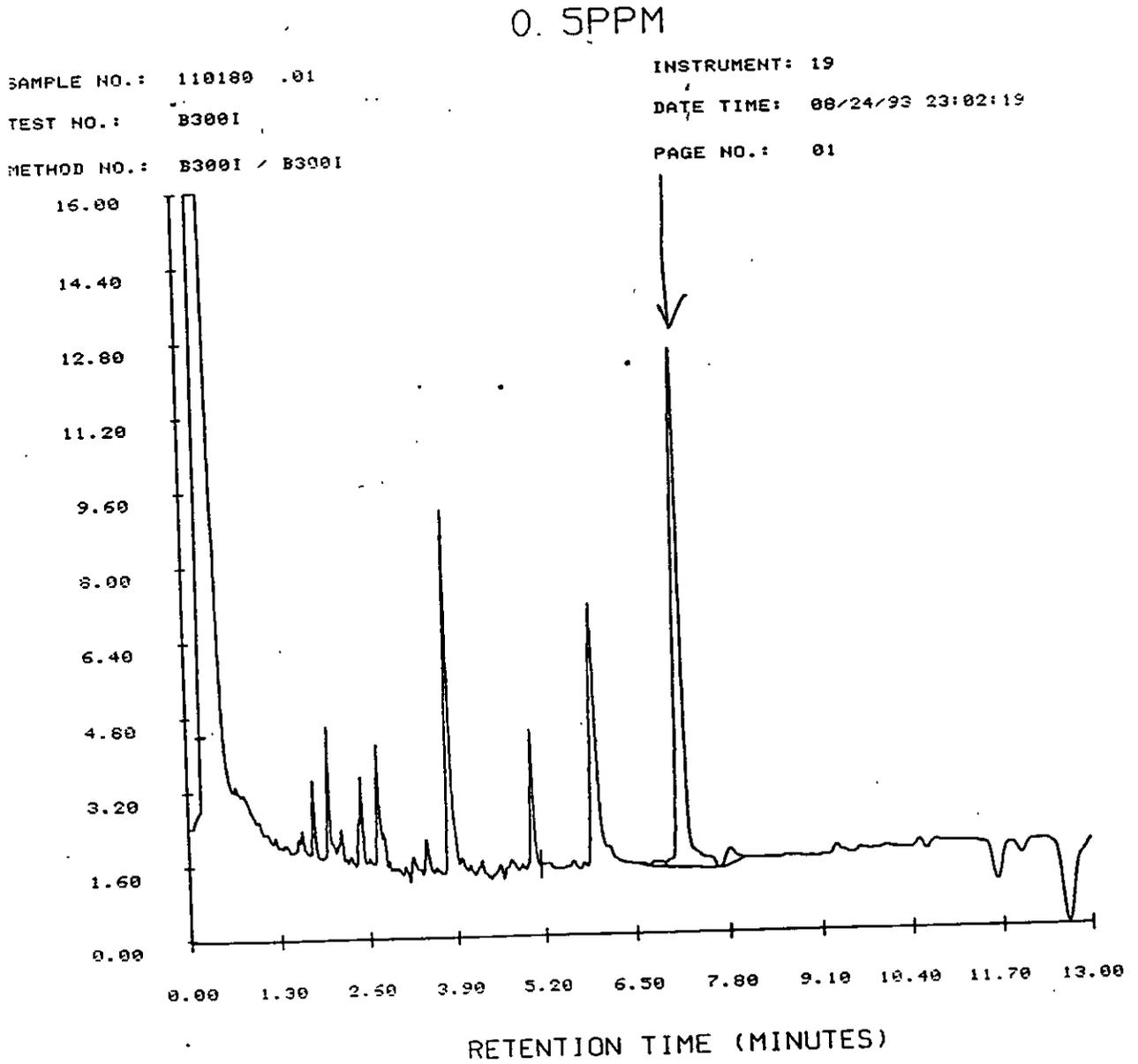
Y MAXIMUM: 53720.

START TIME: 0.00

Y MINIMUM: 51762.

END TIME: 13.00

Figure 35. Chromatogram of a control orange juice sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-11, Sample Number 110180. See Table VI.



Y MAXIMUM: 53502.

Y MINIMUM: 51841.

START TIME: 0.00

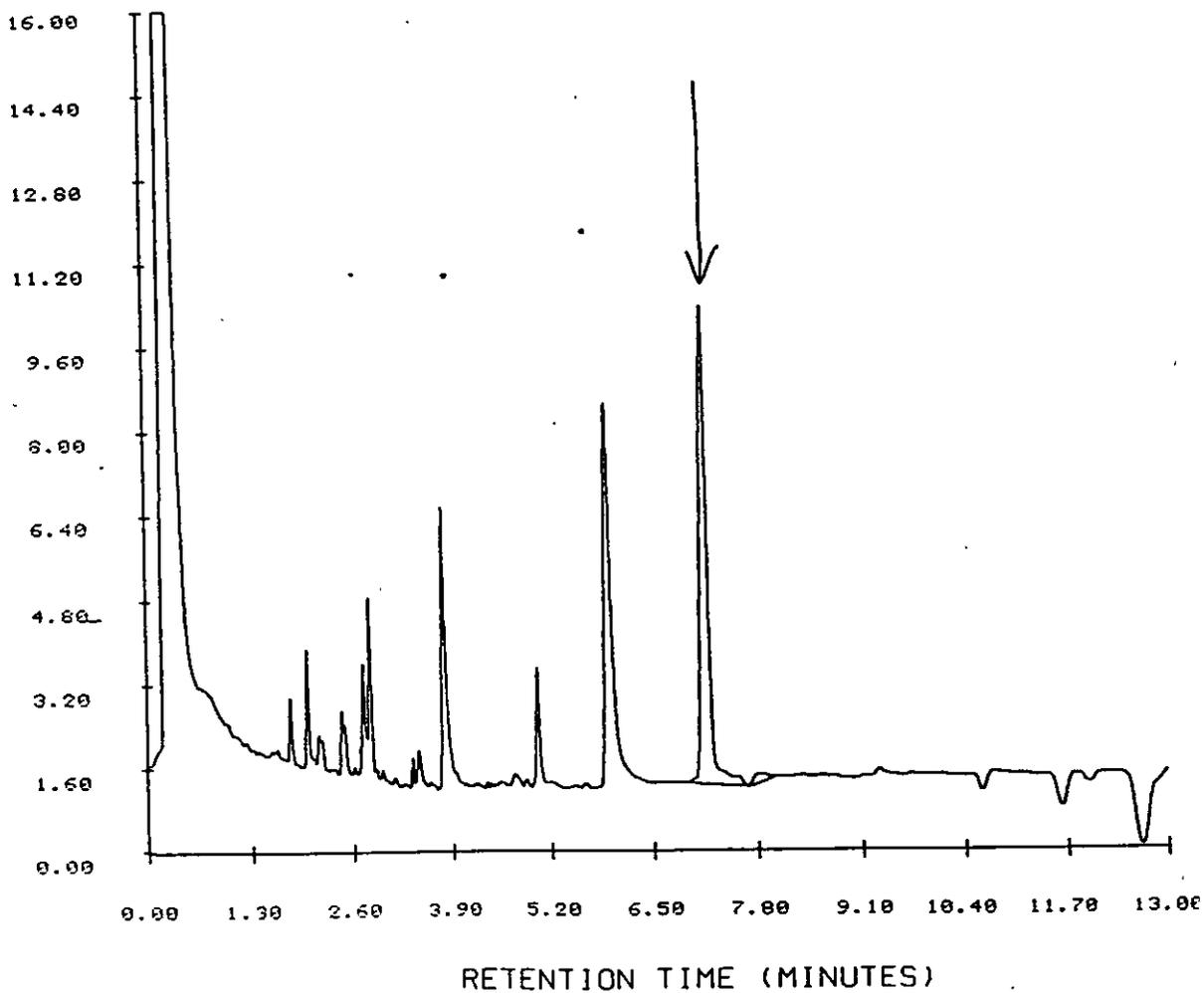
END TIME: 13.00

Figure 36. Chromatogram of a control orange juice sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-11, Sample Number 110181. See Table VI.

0.5PPM

SAMPLE NO.: 110181 .01  
TEST NO.: B300I  
METHOD NO.: B300I / B300I

INSTRUMENT: 19  
DATE TIME: 08/24/93 23:55:45  
PAGE NO.: 01



Y MAXIMUM: 53840.  
Y MINIMUM: 51867.

START TIME: 0.00  
END TIME: 13.00

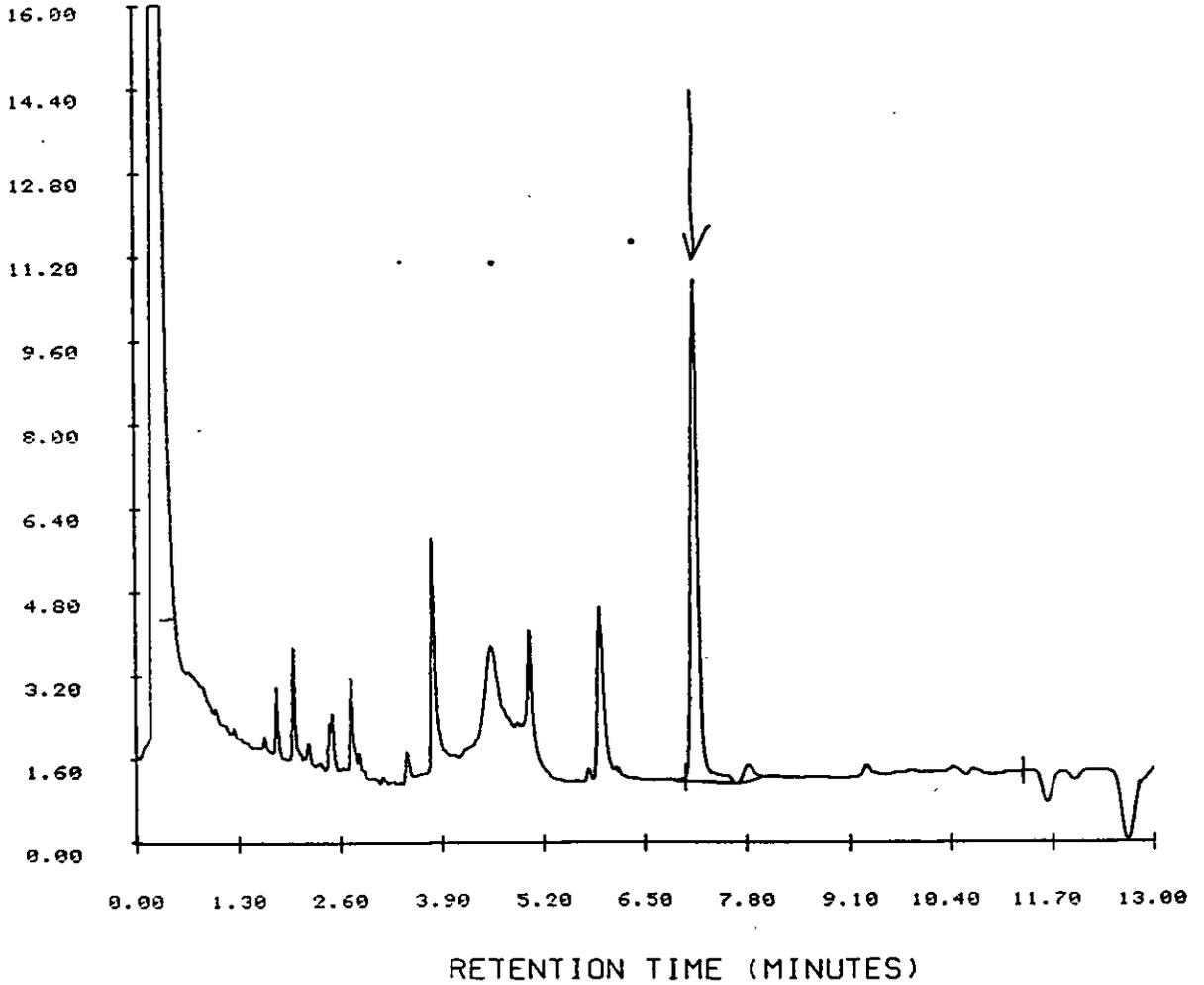
Figure 37.

Chromatogram of a control orange juice sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-11, Sample Number 110182. See Table VI.

0.5PPM

SAMPLE NO.: 110182 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 08/25/93 00:13:32  
PAGE NO.: 01



Y MAXIMUM: 53822.  
Y MINIMUM: 51876.

START TIME: 0.00  
END TIME: 13.00

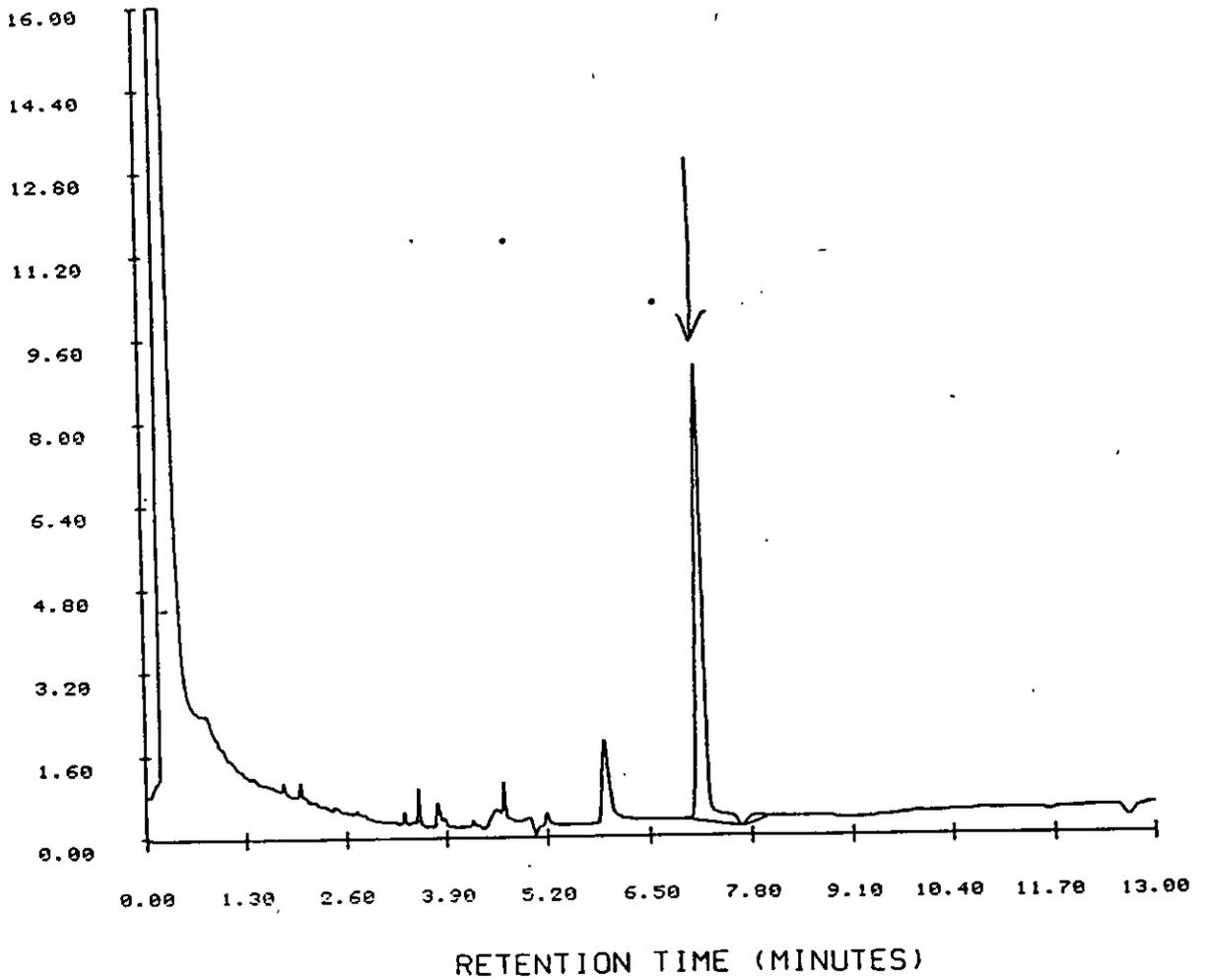
Figure 38.

Chromatogram of a control orange juice sample fortified with 5.0 ppm of BAS 300 I. Master Sheet 93102-11, Sample Number 110183. See Table VI.

### 5.0PPM

SAMPLE NO.: 110183 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / E3001

INSTRUMENT: 19  
DATE TIME: 08/25/93 01:06:53  
PAGE NO.: 01



Y MAXIMUM: 54027.  
Y MINIMUM: 51973.

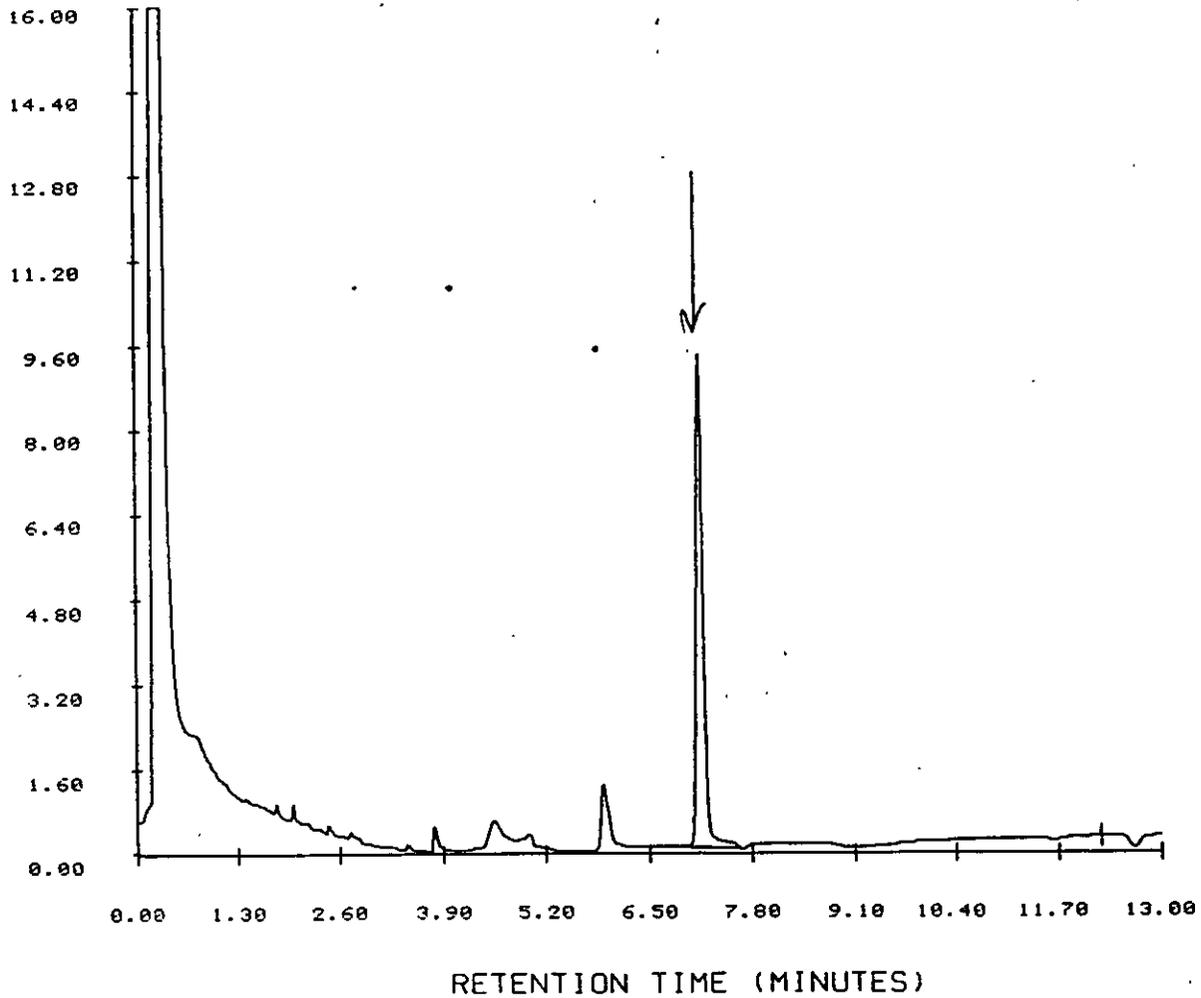
START TIME: 0.00  
END TIME: 13.00

Figure 39. Chromatogram of a control orange juice sample fortified with 5.0 ppm of BAS 300 I. Master Sheet 93102-11, Sample Number 110184. See Table VI.

5.0PPM

SAMPLE NO.: 110184 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 08/25/93 01:24:58  
PAGE NO.: 01



Y MAXIMUM: 53946.  
Y MINIMUM: 51998.

START TIME: 0.00  
END TIME: 13.00

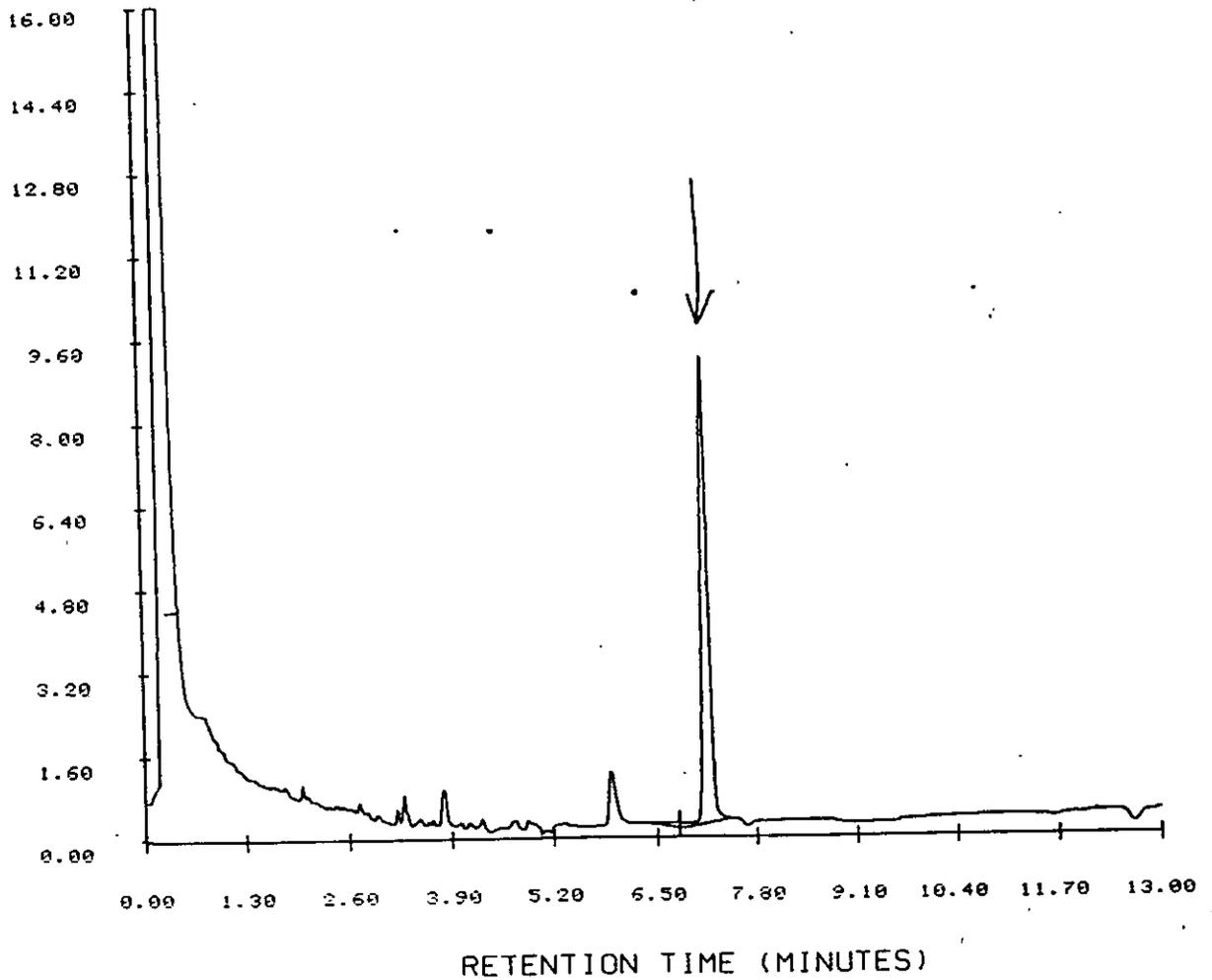
Figure 40.

Chromatogram of a control orange juice sample fortified with 5.0 ppm of BAS 300 I. Master Sheet 93102-11, Sample Number 110185. See Table VI.

5.0PPM

SAMPLE NO.: 110185 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 08/25/93 02:18:20  
PAGE NO.: 01

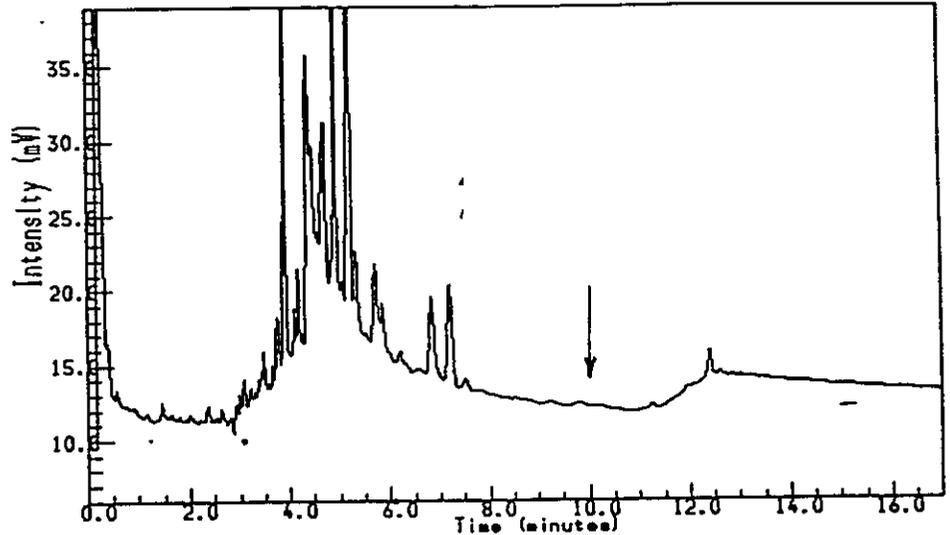


Y MAXIMUM: 54079.  
Y MINIMUM: 51984.

START TIME: 0.00  
END TIME: 13.00

Figure 41. Chromatogram of a control dried orange pulp sample. Master Sheet 93102-22, Sample Number 3. See Table VII.

Acquired on 26-SEP-1993 at 16:29



BASF CORP. - VAX MULTICHROM

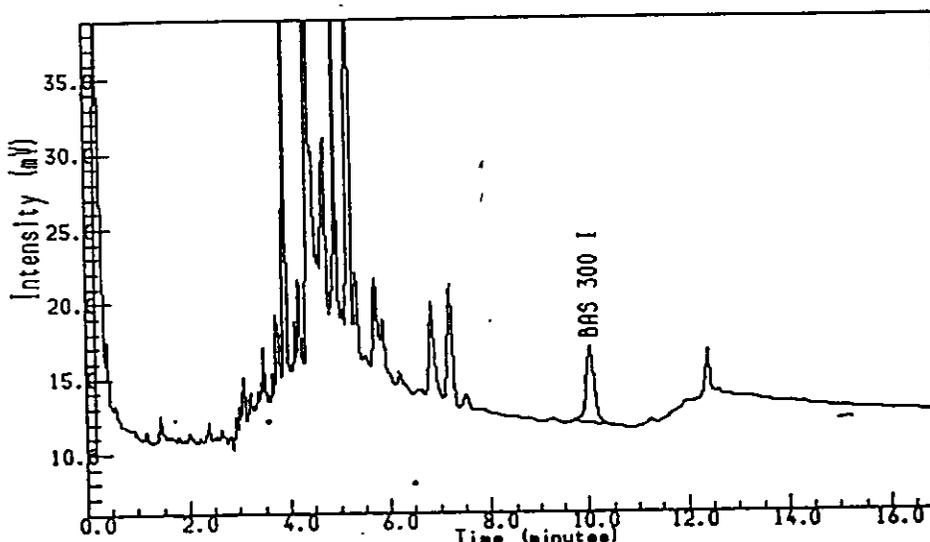
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : CNTRL A PULP  
 Sample Id : 9390201  
 Sample Type : Control Amount=1.00000  
 Bottle No : 3

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
<u>Totals</u>			
Unknowns	0	N/A	
	0	0.000	
	0	0.000	

Figure 42. Chromatogram of a control dried orange pulp sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-22, Sample Number 8. See Table VII.

Acquired on 26-SEP-1993 at 18:19



BASF CORP. - VAX MULTICHROM

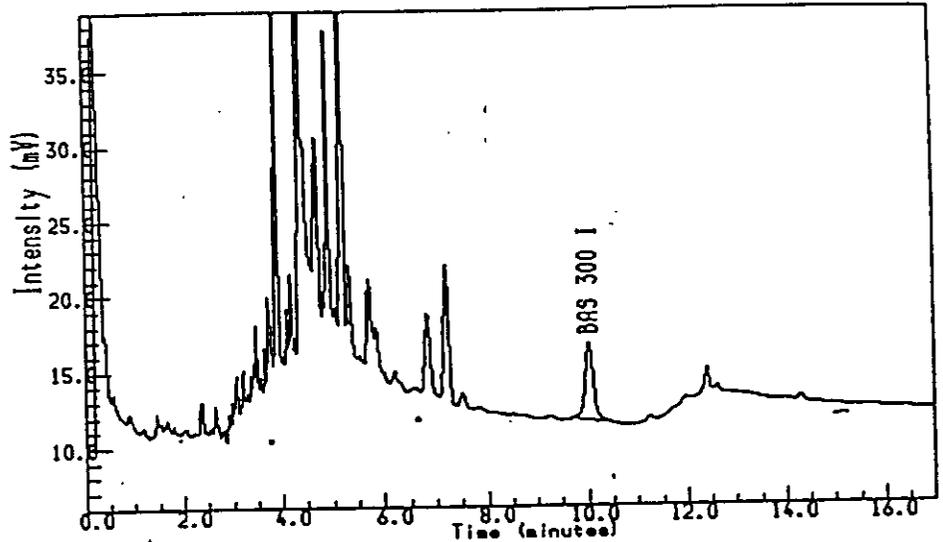
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.05 PPM A PULP  
 Sample Id : 9390201  
 Sample Type : Recovery. Amount=1.00000  
 Bottle No : 8

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.043	5089	42.073	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	5089	42.073	
	5089	42.073	

Figure 43. Chromatogram of a control dried orange pulp sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-22, Sample Number 10. See Table VII.

Acquired on 26-SEP-1993 at 19:02



BASF CORP. - VAX MULTICHROM

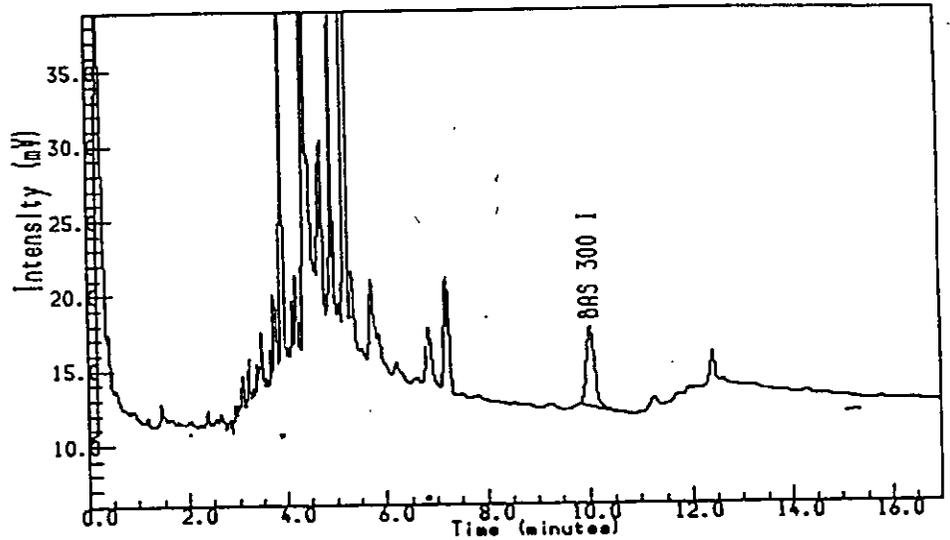
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.05 PPM B PULP  
 Sample Id : 9390201  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 10

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.037	5182	43.003	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	5182	43.003	
	5182	43.003	

Figure 44. Chromatogram of a control dried orange pulp sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-22, Sample Number 13. See Table VII.

Acquired on 26-SEP-1993 at 20:08



BASF CORP. - VAX MULTICHROM

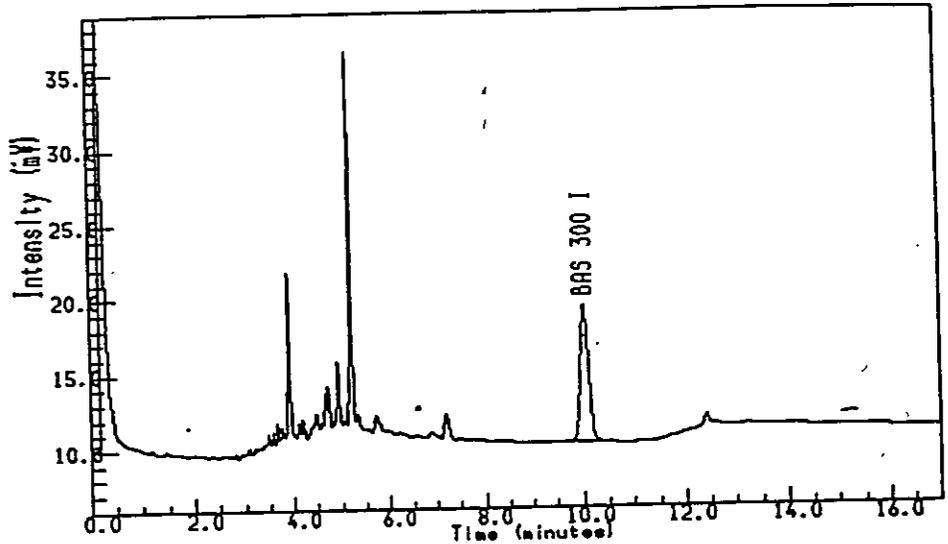
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.05 PPM C PULP  
 Sample Id : 9390201  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 12

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.043	5358	44.762	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	5358	44.762	
	5358	44.762	

Figure 45. Chromatogram of a control dried orange pulp sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-22, Sample Number 15. See Table VII.

Acquired on 26-SEP-1993 at 20:51



BASF CORP. - VAX MULTICHROM

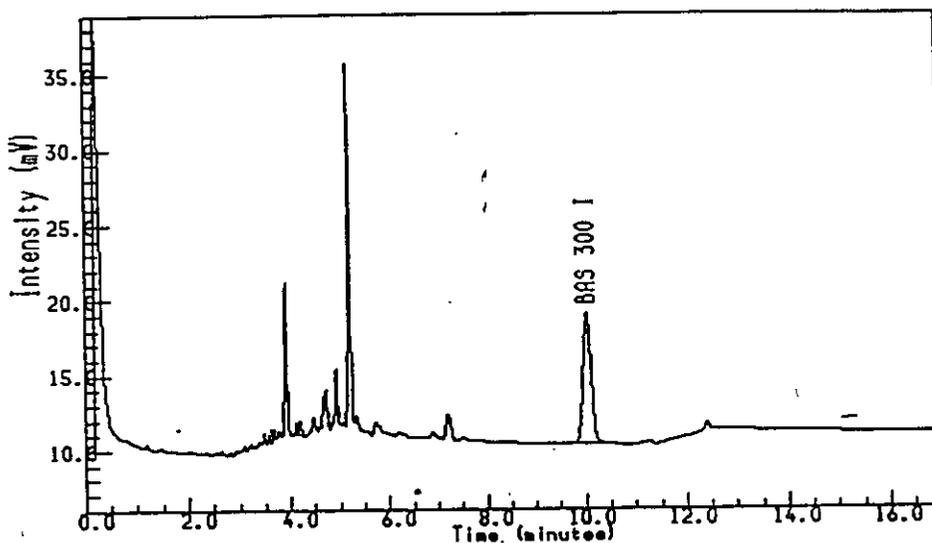
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.50 PPM A PULP  
 Sample Id : 9390201  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 14

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.037	9100	423.128	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	9100	423.128	
	9100	423.128	

Figure 46. Chromatogram of a control dried orange pulp sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-22, Sample Number 18. See Table VII.

Acquired on 26-SEP-1993 at 21:57



BASF CORP. - VAX MULTICHROM

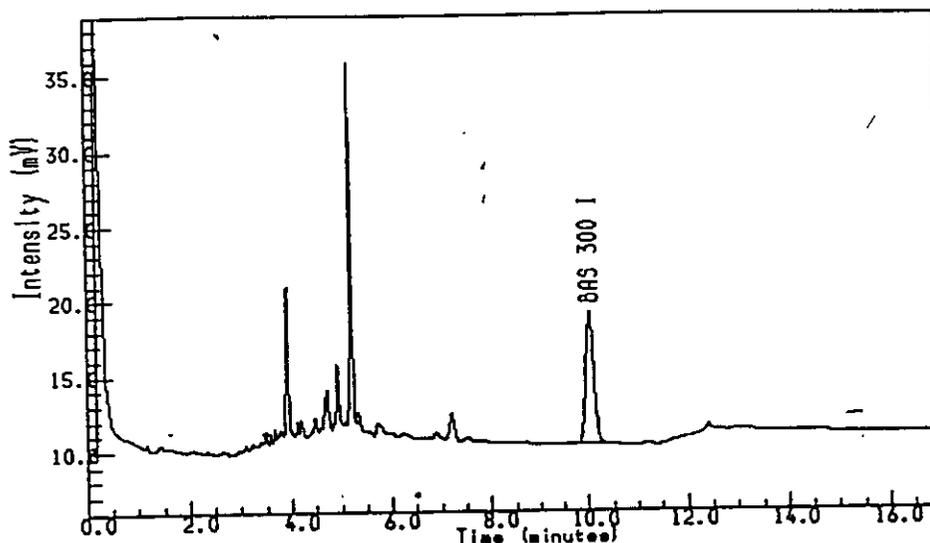
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.50 PPM B PULP  
 Sample Id : 9390201  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 17

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.037	8664	398.865	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	8664	398.865	
	8664	398.865	

Figure 47. Chromatogram of a control dried orange pulp sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-22, Sample Number 19. See Table VII.

Acquired on 26-SEP-1993 at 22:18



BASF CORP. - VAX MULTICHROM

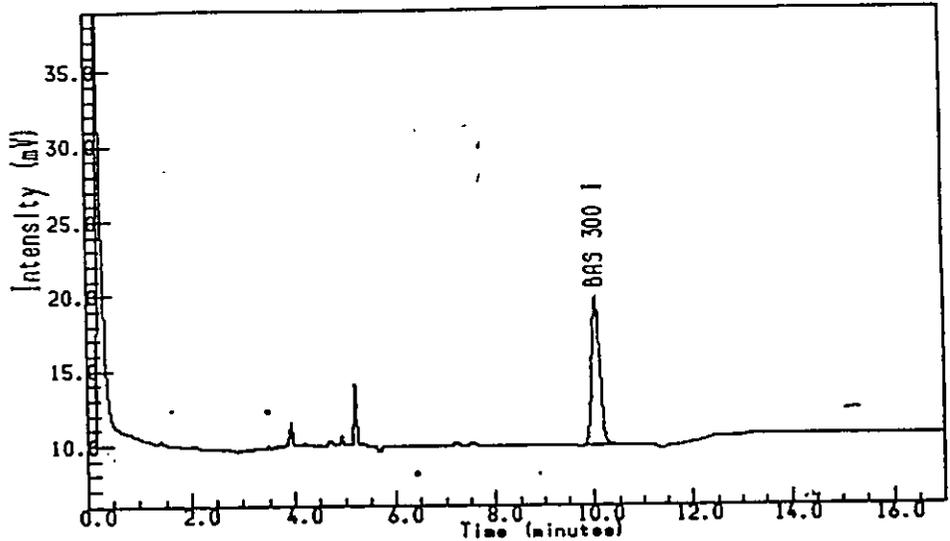
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.50 PPM C PULP  
 Sample Id : 9390201  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 18

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.032	8820	407.503	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	8820	407.503	
	8820	407.503	

Figure 48. Chromatogram of a control dried orange pulp sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-22, Sample Number 22. See Table VII.

Acquired on 26-SEP-1993 at 23:24



BASF CORP. - VAX MULTICHROM

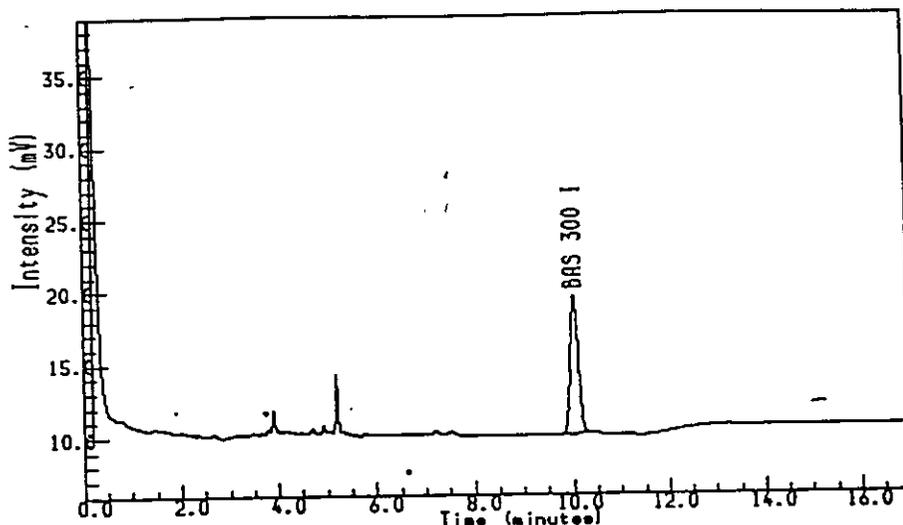
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 5.0 PPM A PULP  
 Sample Id : 9390201  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 21

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.053	9924	4696.005	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	9924	4696.005	
	9924	4696.005	

Figure 50. Chromatogram of a control dried orange pulp sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-22, Sample Number 26. See Table VII.

Acquired on 27-SEP-1993 at 00:51



BASF CORP. - VAX MULTICHROM

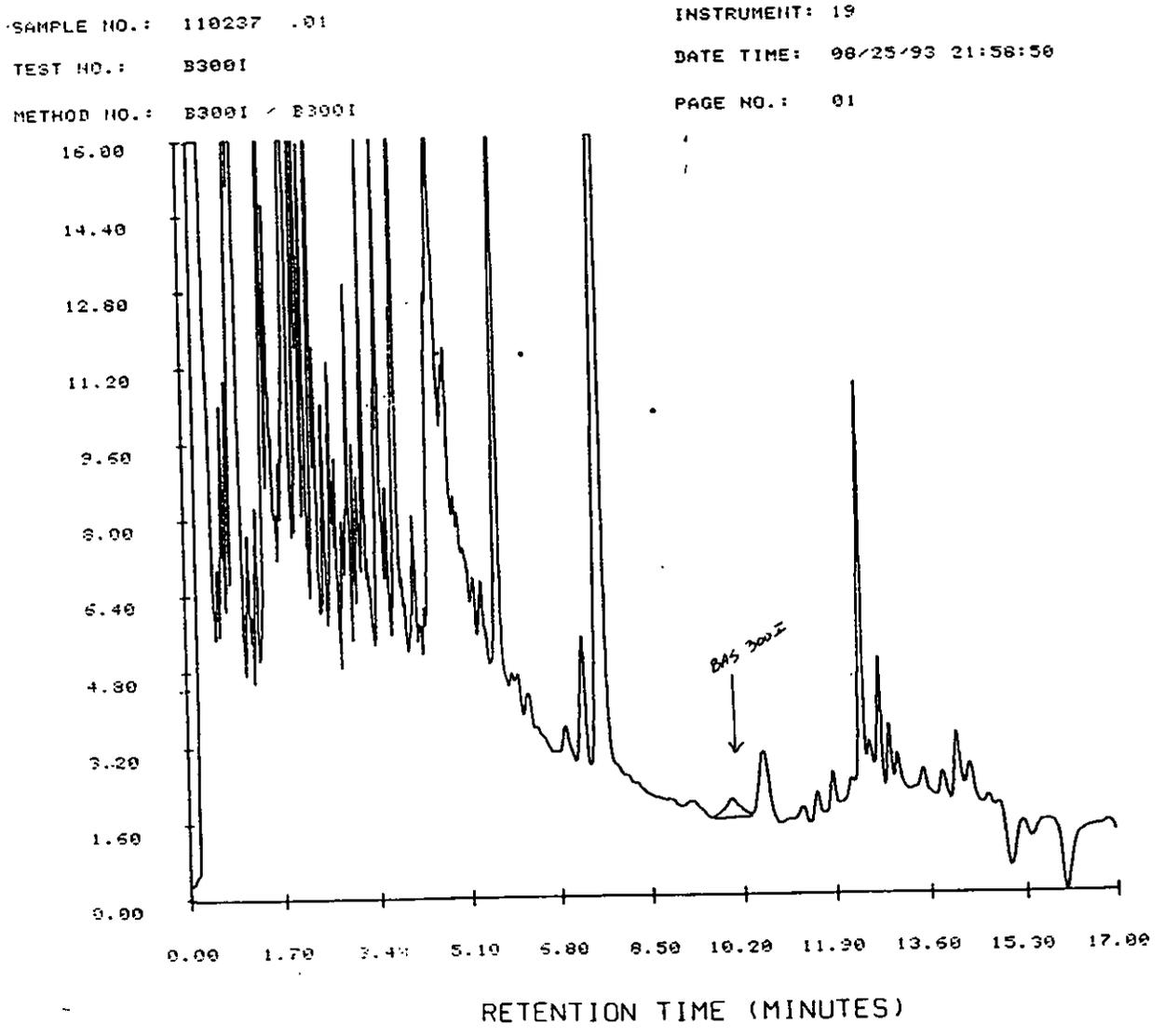
Analyst Name : ERIC HESS  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 5.0 PPM C PULP  
 Sample Id : 9390201  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 25

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.037	9519	4466.311	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	9519	4466.311	
	9519	4466.311	

Figure 51. Chromatogram of a control orange molasses sample. Master Sheet 93102-12, Sample Number 110237. See Table VIII.

### CONTROL A MOLASSES



SAMPLE NO.: 110237 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 08/25/93 21:58:50  
PAGE NO.: 01

Y MAXIMUM: 54410.  
Y MINIMUM: 51825.

START TIME: 0.00  
END TIME: 17.00

Figure 52.

Chromatogram of a control orange molasses sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-12, Sample Number 110239. See Table VIII.

### 0.05 PPM A MOLASSES

SAMPLE NO.: 110239 .01

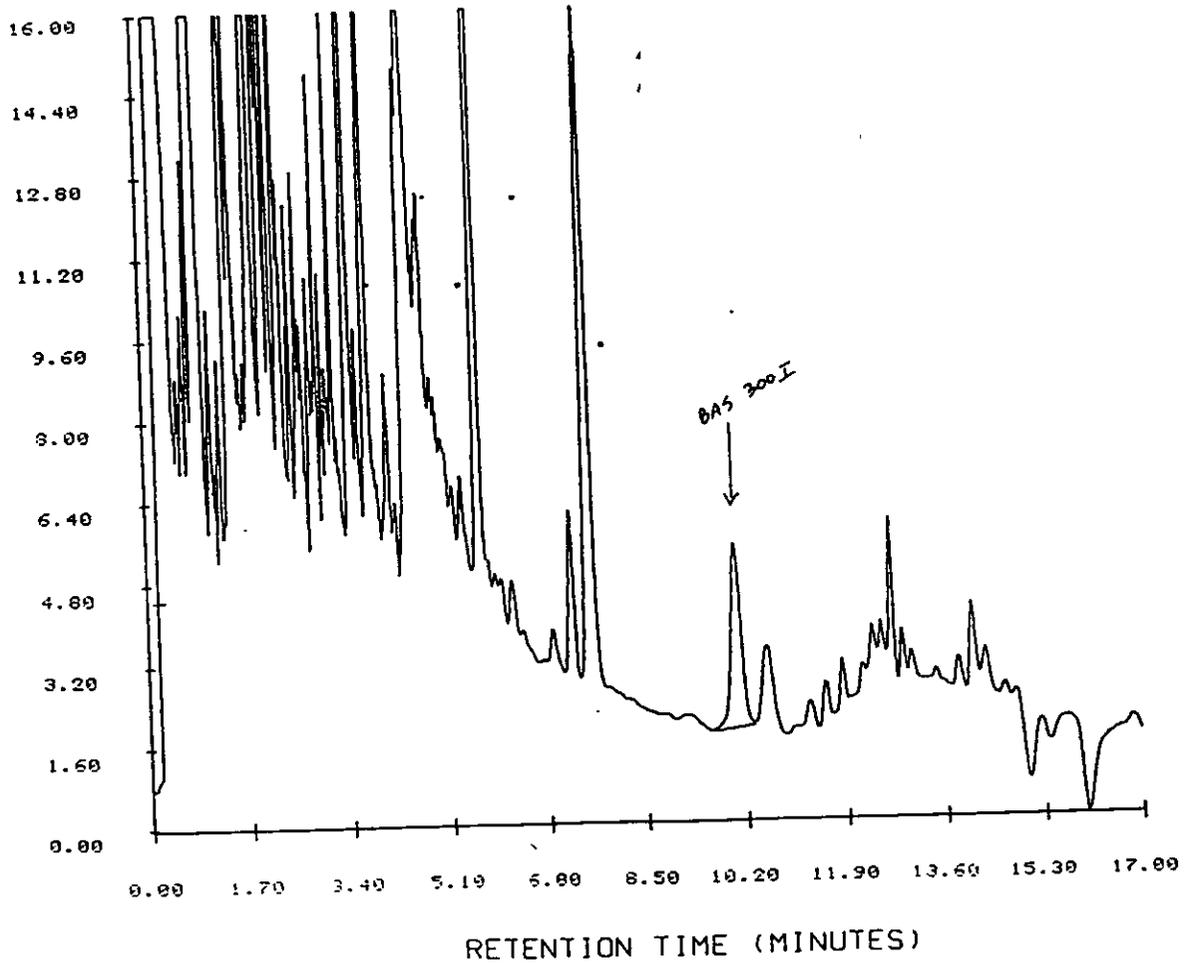
INSTRUMENT: 19

TEST NO.: 93001

DATE TIME: 08/25/93 23:59:17

METHOD NO.: 93001 / 93001

PAGE NO.: 01



Y MAXIMUM: 53216.

START TIME: 0.00

Y MINIMUM: 51747.

END TIME: 17.00





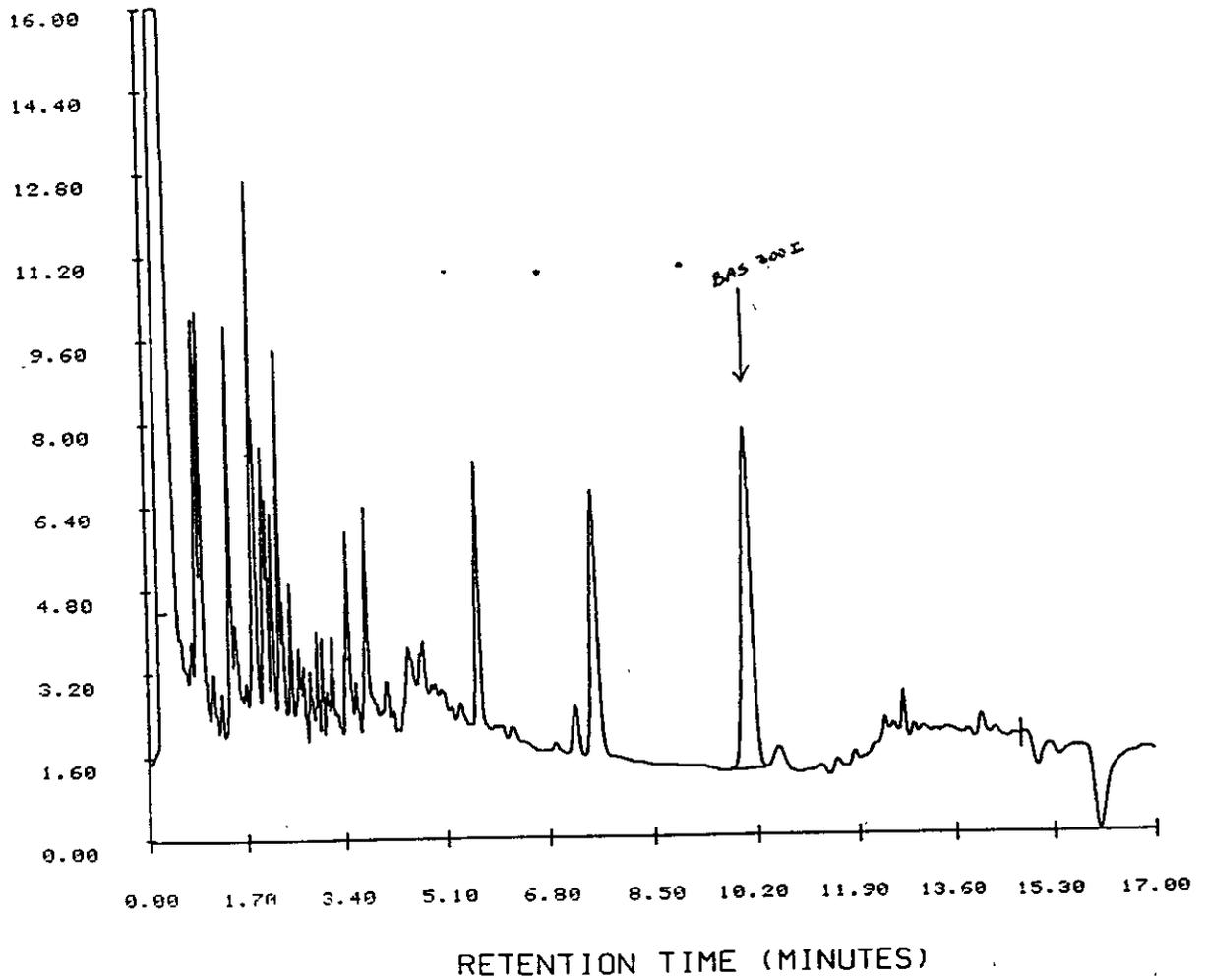
Figure 55.

Chromatogram of a control orange molasses sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-12, Sample Number 110242. See Table VIII.

### 0.50 PPM A MOLASSES

SAMPLE NO.: 110242 .01  
TEST NO.: 53001  
METHOD NO.: B3001 / 53001

INSTRUMENT: 19  
DATE TIME: 08/26/93 02:33:54  
PAGE NO.: 01



Y MAXIMUM: 53629.  
Y MINIMUM: 51723.

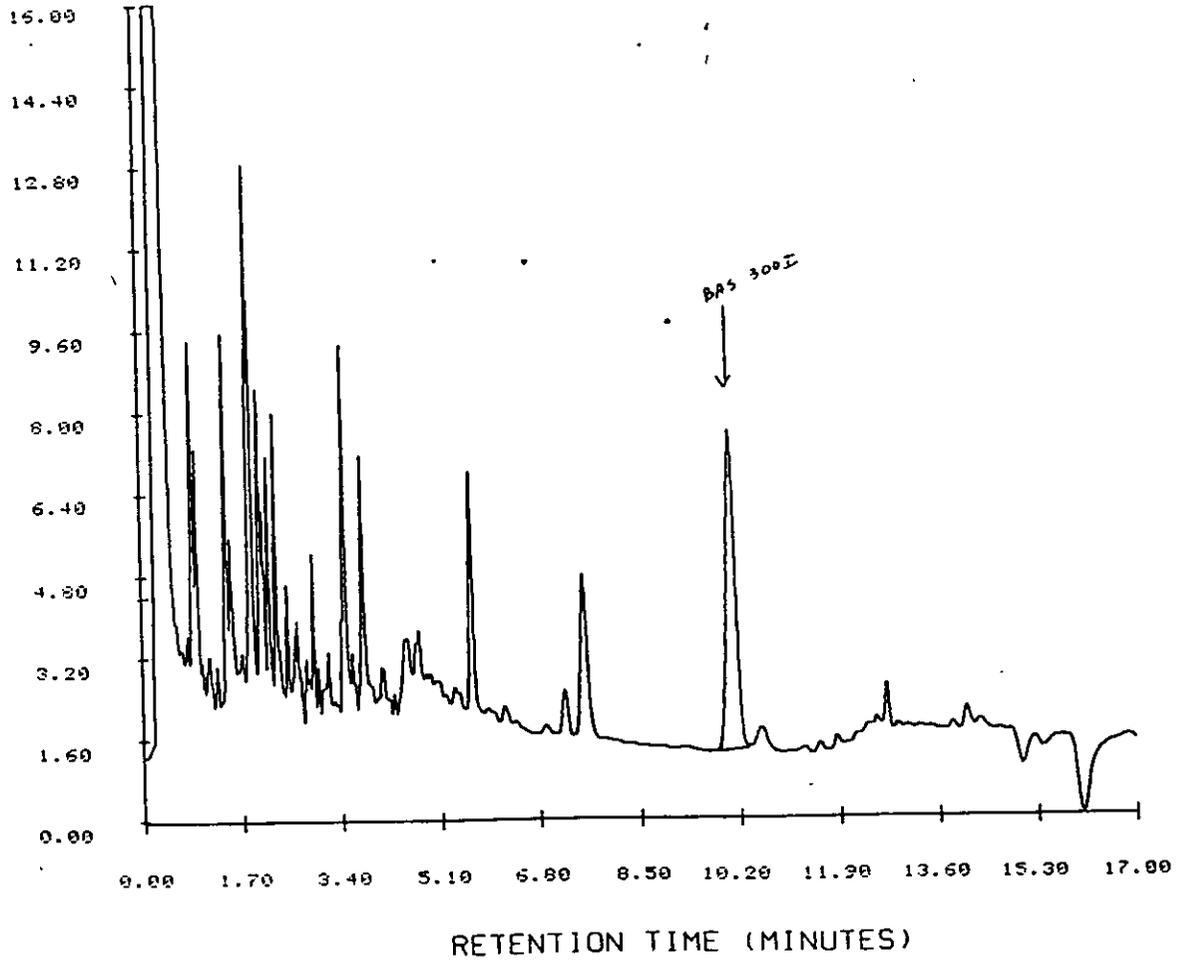
START TIME: 0.00  
END TIME: 17.00

Figure 56. Chromatogram of a control orange molasses sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-12, Sample Number 110243. See Table VIII.

### 0.50 PPM B MOLASSES

SAMPLE NO.: 110243 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 19  
DATE TIME: 08/26/90 03:39:15  
PAGE NO.: 01



Y MAXIMUM: 53703.  
Y MINIMUM: 51691.

START TIME: 0.00  
END TIME: 17.00

Figure 57.

Chromatogram of a control orange molasses sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-12, Sample Number 110244. See Table VIII.

### 0.50 PPM C MOLASSES

SAMPLE NO.: 110244 .01

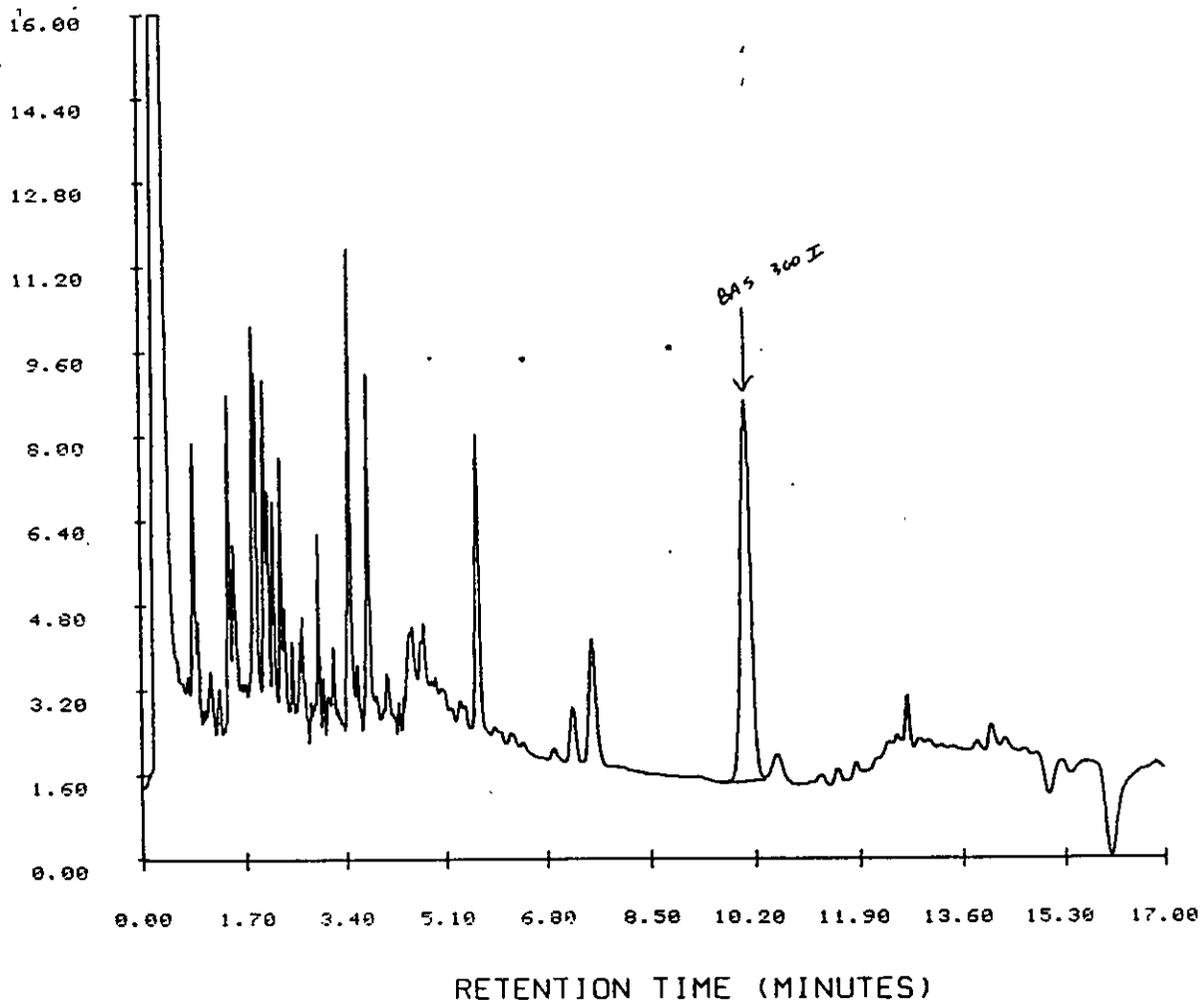
INSTRUMENT: 19

TEST NO.: B3001

DATE TIME: 08/26/93 04:01:02

METHOD NO.: B3001 / B3001

PAGE NO.: 01



Y MAXIMUM: 53421.

START TIME: 0.00

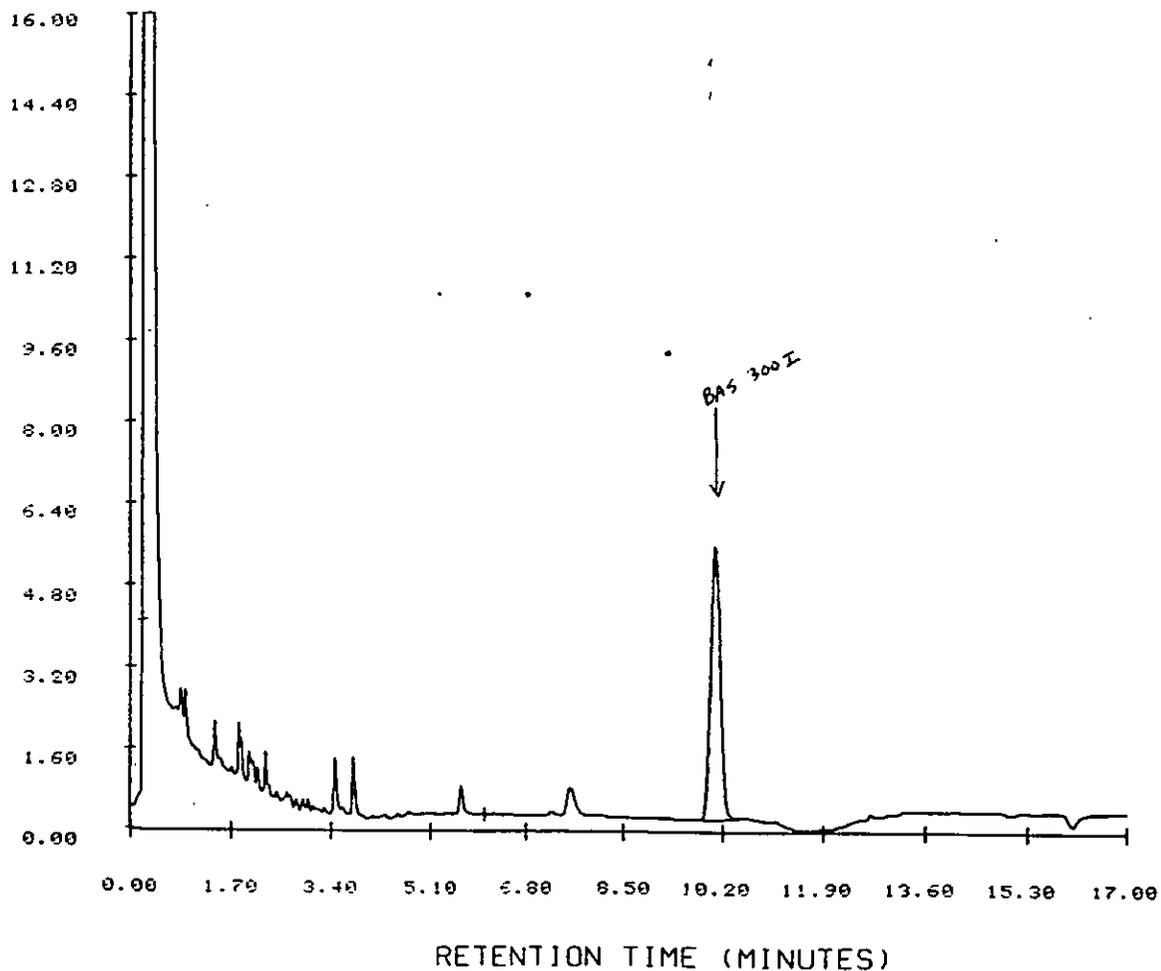
Y MINIMUM: 51707.

END TIME: 17.00

Figure 58. Chromatogram of a control orange molasses sample fortified with 5.0 ppm of BAS 300 I. Master Sheet 93102-12, Sample Number 110245. See Table VIII.

### 5.0 PPM A MOLASSES

SAMPLE NO.: 110245 .01                      INSTRUMENT: 19  
TEST NO.: B3001                                DATE TIME: 08/26/93 14:35:42  
METHOD NO.: B3001 / B3001                    PAGE NO.: 01



Y MAXIMUM: 53825.                                START TIME: 0.00  
Y MINIMUM: 51757.                                END TIME: 17.00

Figure 59. Chromatogram of a control orange molasses sample fortified with 5.0 ppm of BAS 300 I. Master Sheet 93102-12, Sample Number 110246. See Table VIII.

PERKIN ELMER CORP PART NO N625-1026

3C

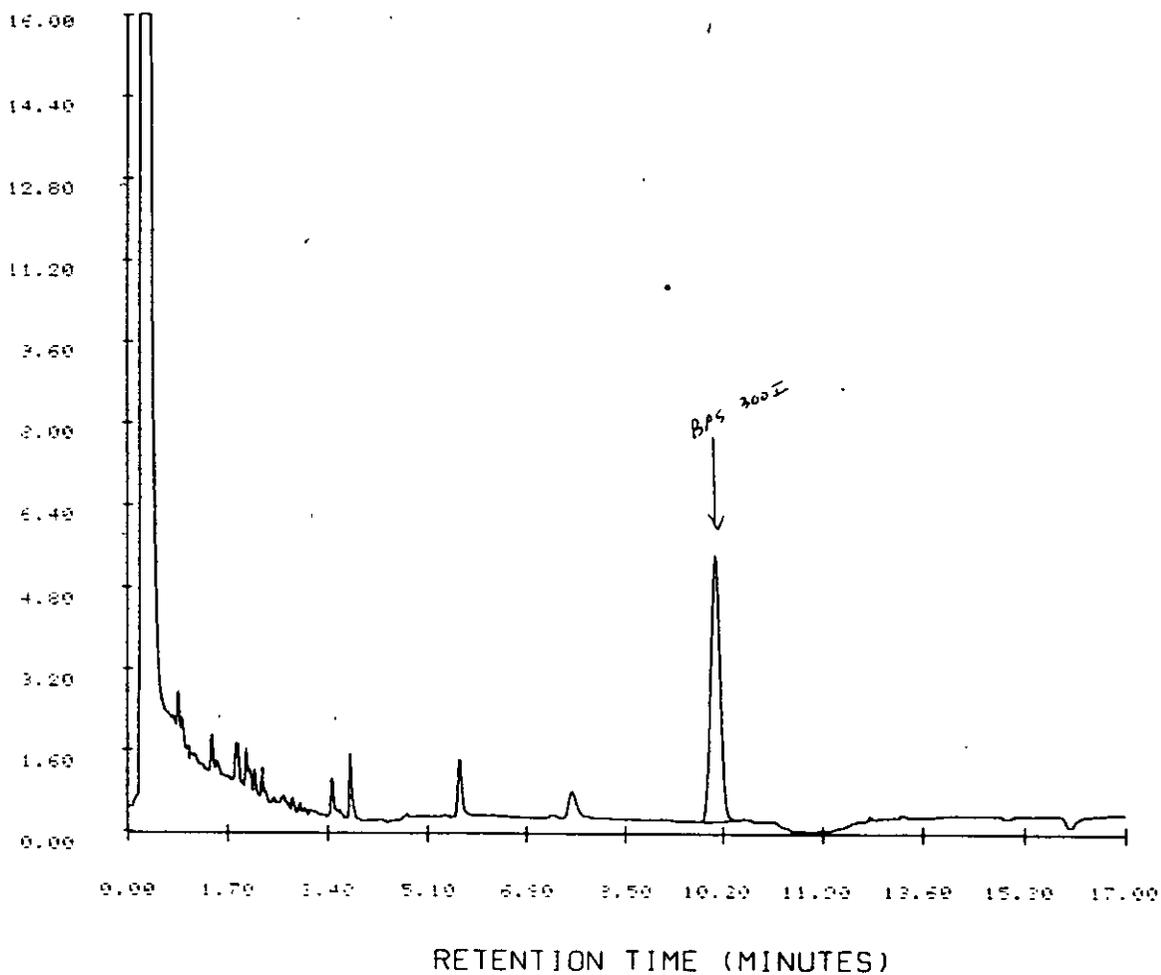
026

PERKIN-E

### 5.0 PPM B MOLASSES

SAMPLE NO.: 110246 .01  
TEST NO.: B3001  
METHOD NO.: B3001 B3001

INSTRUMENT: 19  
DATE TIME: 08-26-93 15:01:22  
PAGE NO.: 01



Y MAXIMUM: 53903.  
Y MINIMUM: 51753.

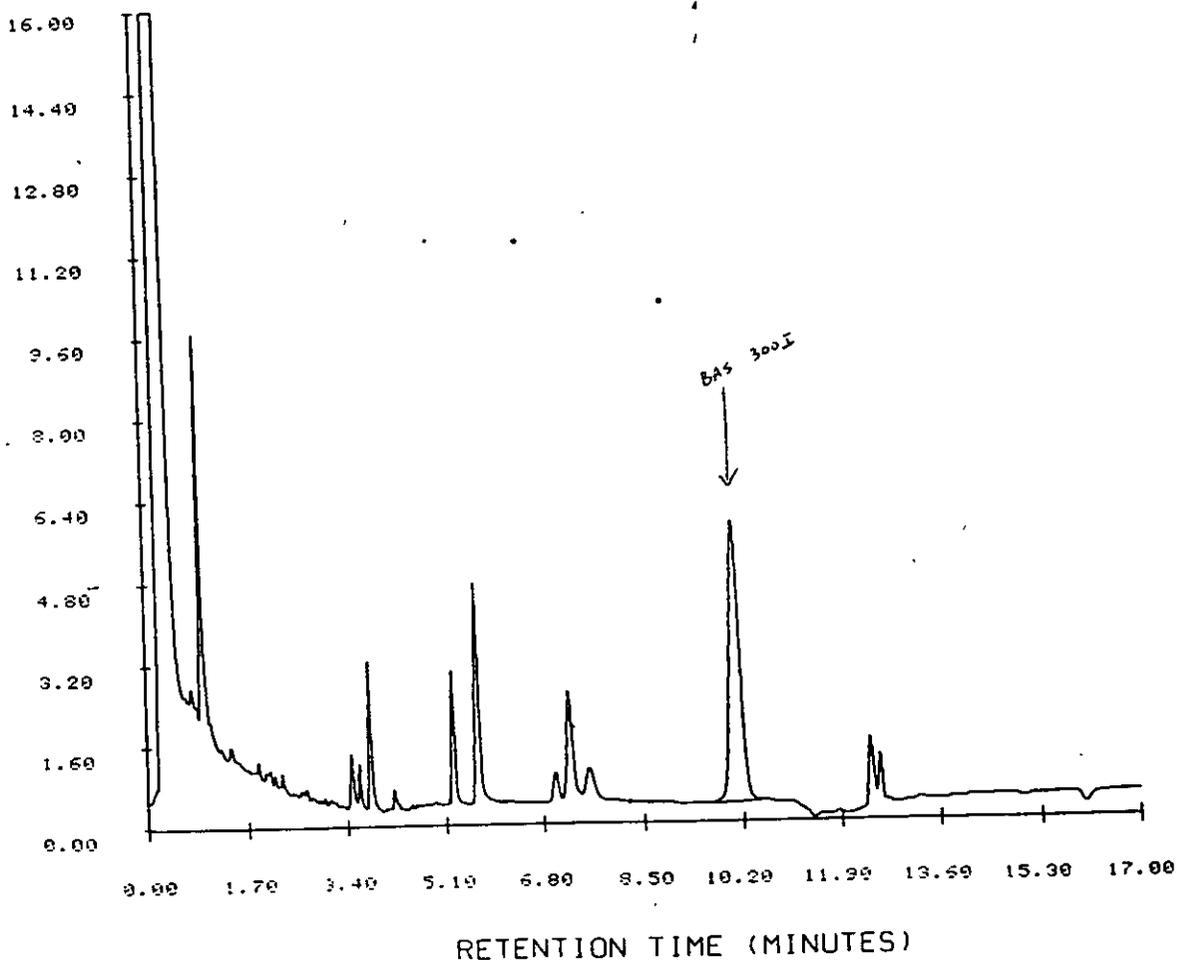
START TIME: 0.00  
END TIME: 17.00

Figure 60. Chromatogram of a control orange molasses sample fortified with 5.0 ppm of BAS 300 I. Master Sheet 93102-12, Sample Number 110247. See Table VIII.

### 5.0 PPM C MOLASSES

SAMPLE NO.: 110247 .01  
TEST NO.: B3001  
METHOD NO.: B3001 / B3001

INSTRUMENT: 13  
DATE TIME: 08/25/93 16:42:57  
PAGE NO.: 01

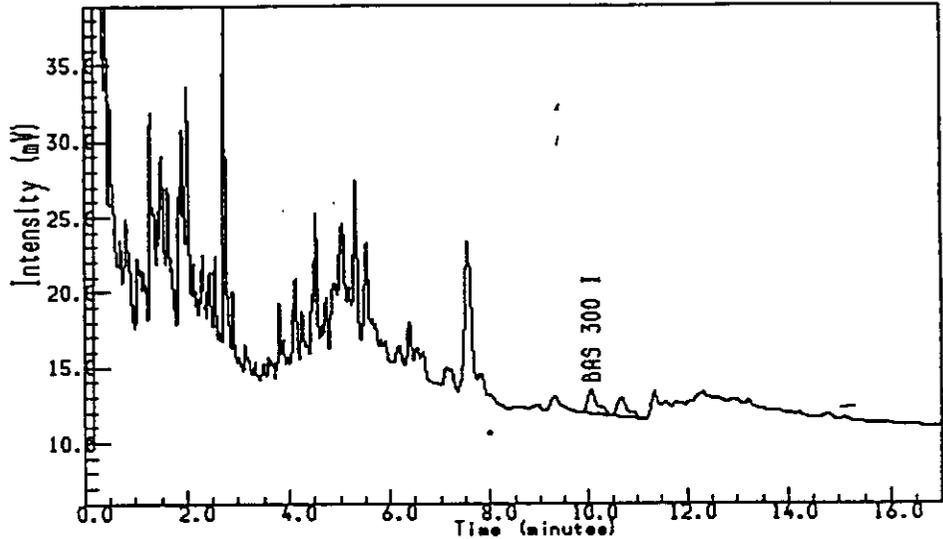


MAXIMUM: 53702.  
MINIMUM: 51736.

START TIME: 0.00  
END TIME: 17.00

Figure 61. Chromatogram of a control orange oil sample. Master Sheet 93102-21, Sample Number 3. See Table IX.

Acquired on 24-SEP-1993 at 16:07



BASF CORP. - VAX MULTICHROM

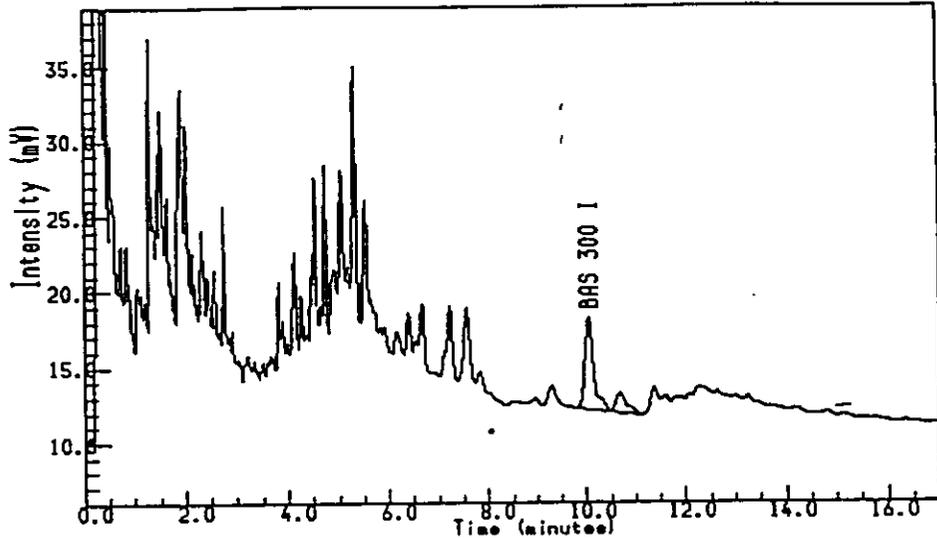
Analyst Name : SCOTT MALINSKY  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : CNTRL OIL A  
 Sample Id : 9390602  
 Sample Type : Control Amount=1.00000  
 Bottle No : 3

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.053	1555	8.314	BAS 300 I
10.688	1272	0.000	
<u>Totals</u>			
Unknowns	0	N/A	
	2827	8.314	
	2827	8.314	

Figure 62. Chromatogram of a control orange oil sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-21, Sample Number 8. See Table IX.

Acquired on 24-SEP-1993 at 17:56



BASF CORP. - VAX MULTICHROM

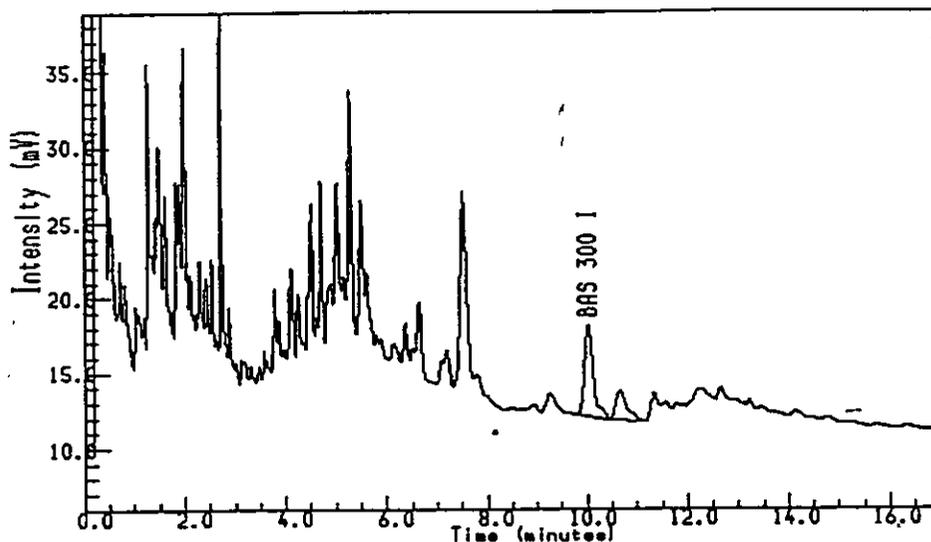
Analyst Name : SCOTT MALINSKY  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.05PPM A  
 Sample Id : 9390602  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 8

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.059	6059	50.652	BAS 300 I
10.688	1282	0.000	
<u>Totals</u>			
Unknowns	0	N/A	
	7341	50.652	
	7341	50.652	

Figure 63. Chromatogram of a control orange oil sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-21, Sample Number 10. See Table IX.

Acquired on 24-SEP-1993 at 18:39



BASF CORP. - VAX MULTICHROM

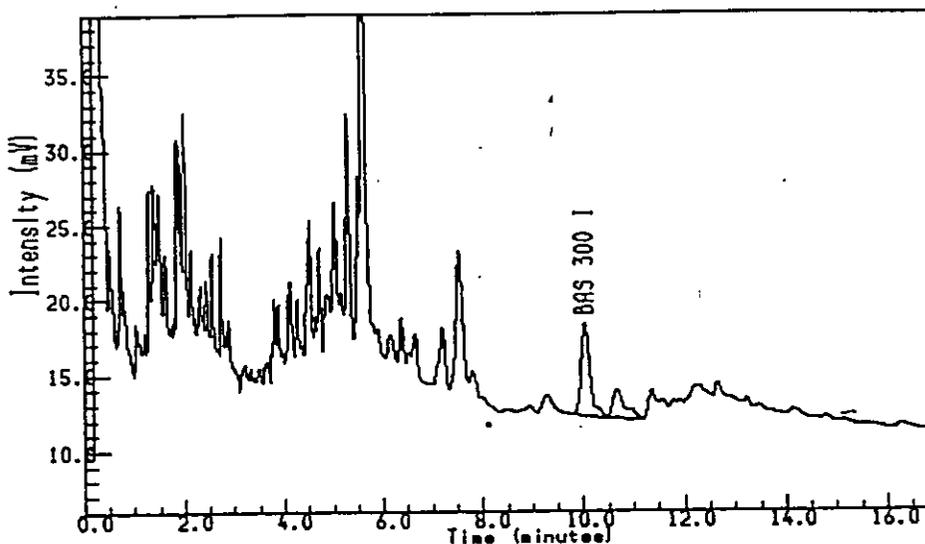
Analyst Name : SCOTT MALINSKY  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.05PPM B  
 Sample Id : 9390602  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 10

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.037	6067	50.738	BAS 300 I
10.672	1953	0.000	
<u>Totals</u>			
Unknowns	0	N/A	
	8020	50.738	
	8020	50.738	

Figure 64. Chromatogram of a control orange oil sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. Master Sheet 93102-21, Sample Number 13. See Table IX.

Acquired on 24-SEP-1993 at 19:45



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.05PPM C  
 Sample Id : 9390602  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 12

PEAK INFORMATION

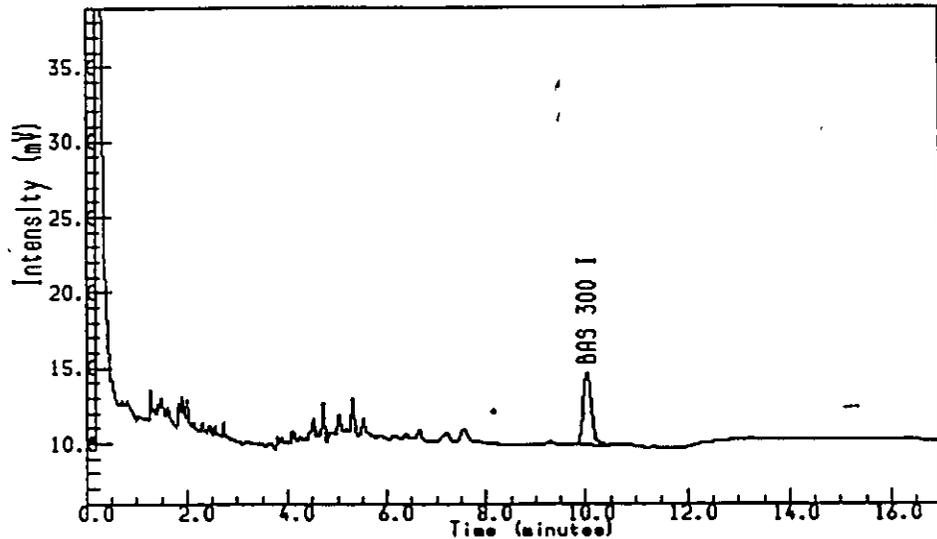
RT mins	Hght uV	ppb	Peak name
10.043	6070	50.777	BAS 300 I
10.667	1887	0.000	

Totals

Unknowns	0	N/A
	7958	50.777
	7958	50.777

Figure 65. Chromatogram of a control orange oil sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-21, Sample Number 15. See Table IX.

Acquired on 24-SEP-1993 at 20:28



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.5PPM A  
 Sample Id : 9390602  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 14

PEAK INFORMATION

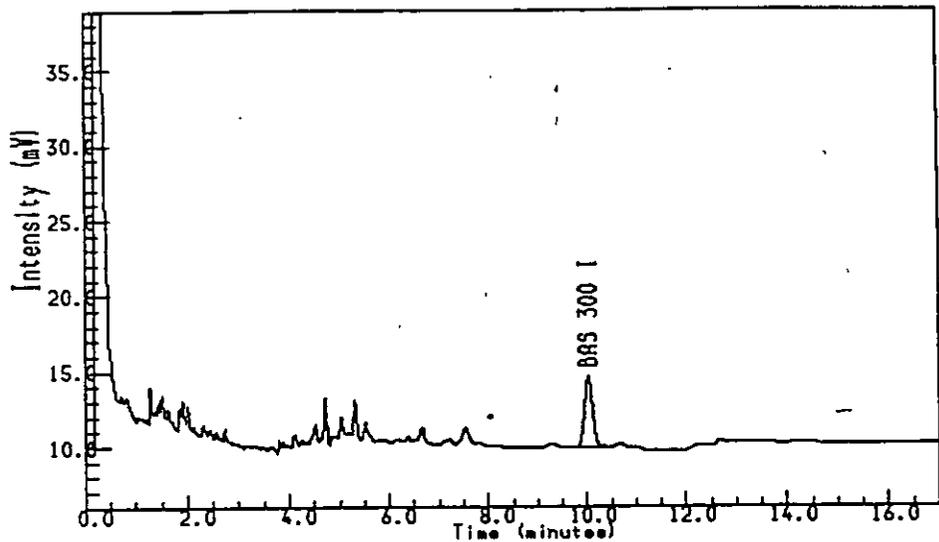
RT mins	Hght uV	ppb	Peak name
10.037	4832	468.751	BAS 300 I

Totals

Unknowns	0	N/A
	4832	468.751
	4832	468.751

Figure 66. Chromatogram of a control orange oil sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-21, Sample Number 18. See Table IX.

Acquired on 24-SEP-1993 at 21:34



BASF CORP. - VAX MULTICHROM

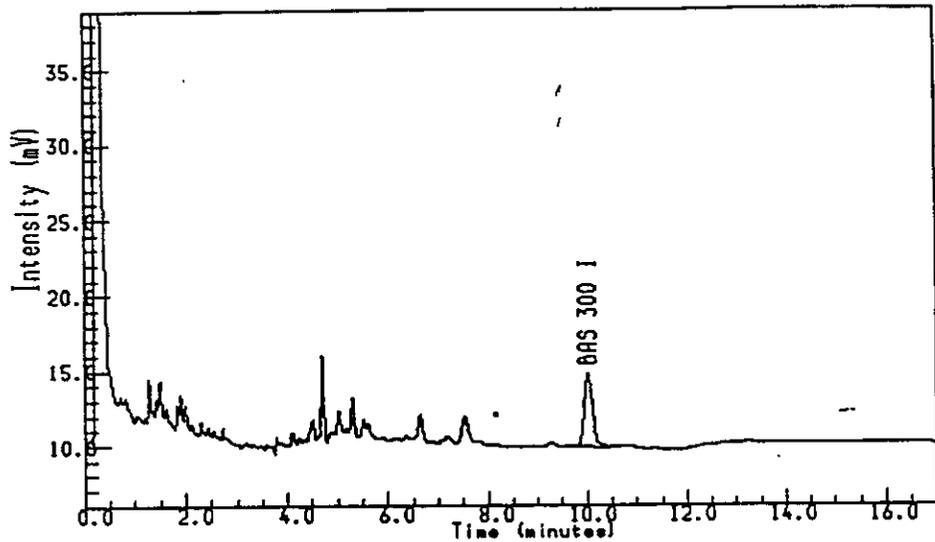
Analyst Name : SCOTT MALINSKY  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.5PPM B  
 Sample Id : 9390602  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 17

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.043	4837	469.429	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	4837	469.429	
	4837	469.429	

Figure 67. Chromatogram of a control orange oil sample fortified with 0.50 ppm of BAS 300 I. Master Sheet 93102-21, Sample Number 19. See Table IX.

Acquired on 24-SEP-1993 at 21:56



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 0.5PPM C  
 Sample Id : 9390602  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 18

PEAK INFORMATION

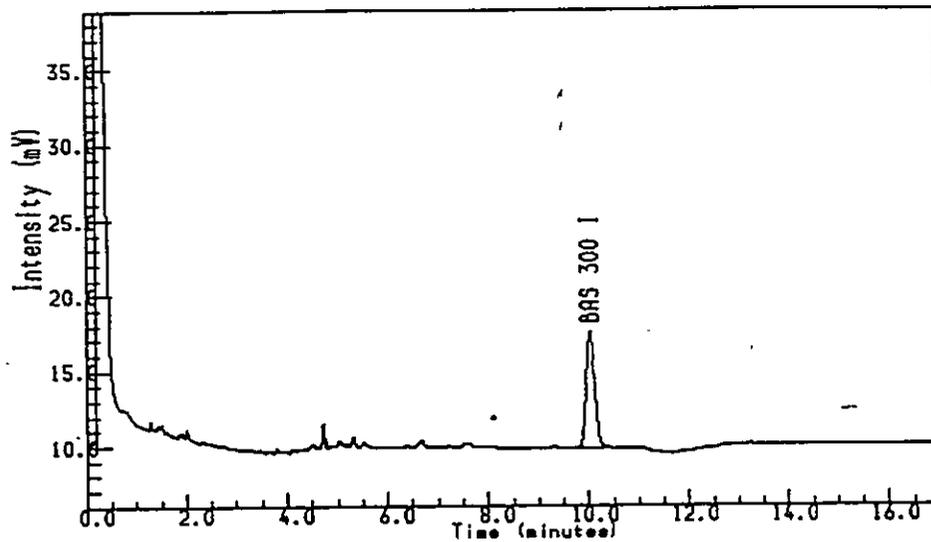
RT mins	Hght uV	ppb	Peak name
10.037	4870	473.656	BAS 300 I

Totals

Unknowns	0	N/A
	4870	473.656
	4870	473.656

Figure 68. Chromatogram of a control orange oil sample fortified with 5.0 ppm of BAS 300 I. Master Sheet 93102-21, Sample Number 22. See Table IX.

Acquired on 24-SEP-1993 at 23:01



BASF CORP. - VAX MULTICHROM

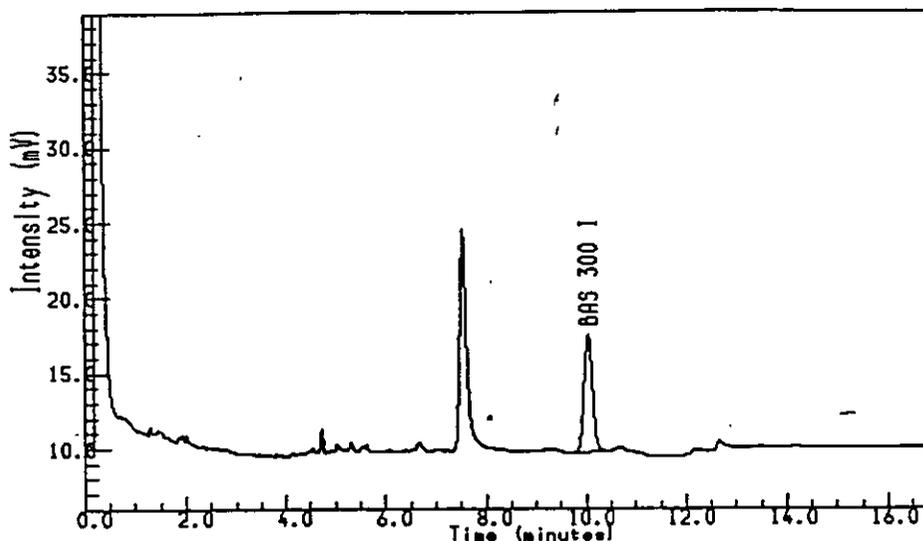
Analyst Name : SCOTT MALINSKY  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 5.0PPM A  
 Sample Id : 9390602  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 21

PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.043	7732	4376.545	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	7732	4376.545	
	7732	4376.545	

Figure 69. Chromatogram of a control orange oil sample fortified with 5.0 ppm of BAS 300 I. Master Sheet 93102-21, Sample Number 23. See Table IX.

Acquired on 24-SEP-1993 at 23:23



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 5.0PPM B  
 Sample Id : 9390602  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 22

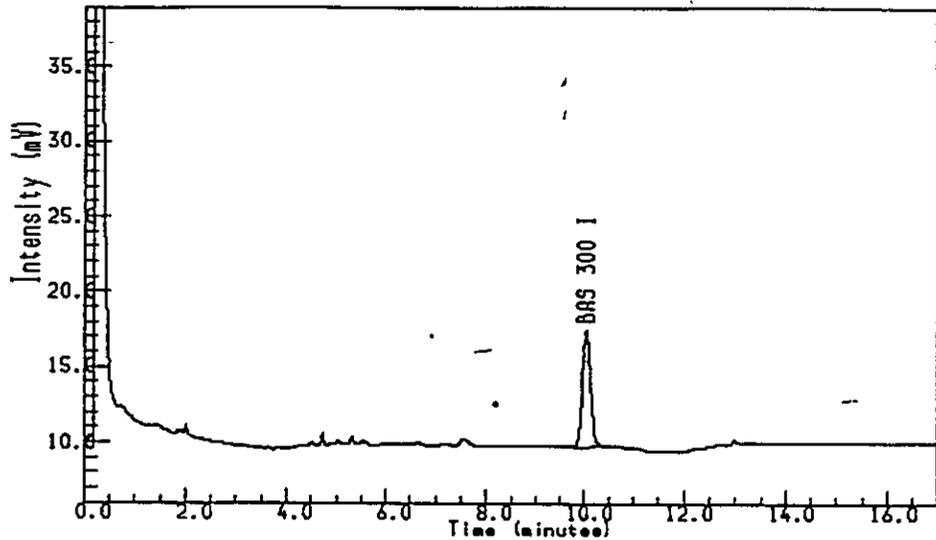
PEAK INFORMATION

RT mins	Hght uV	ppb	Peak name
10.048	7867	4478.549	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	7867	4478.549	
	7867	4478.549	

Figure 70.

Chromatogram of a control orange oil sample fortified with 5.0 ppm of BAS 300 I. Master Sheet 93102-21, Sample Number 26. See Table IX.

Acquired on 25-SEP-1993 at 00:28



BASF CORP. - VAX MULTICHROM

Analyst Name : SCOTT MALINSKY  
 Lims Id :  
 Comment :  
 Method Title : METHOD FOR PYRIDABEN (BAS 300I)  
 Sample Name : 5.0PPM C  
 Sample Id : 9390602  
 Sample Type : Recovery Amount=1.00000  
 Bottle No : 25

PEAK INFORMATION

RT mins	Hqht uV	ppb	Peak name
10.037	7749	4389.345	BAS 300 I
<u>Totals</u>			
Unknowns	0	N/A	
	7749	4389.345	
	7749	4389.345	

Figure 71. Typical GC/MS standard chromatogram (100 pg of BAS 300 I).

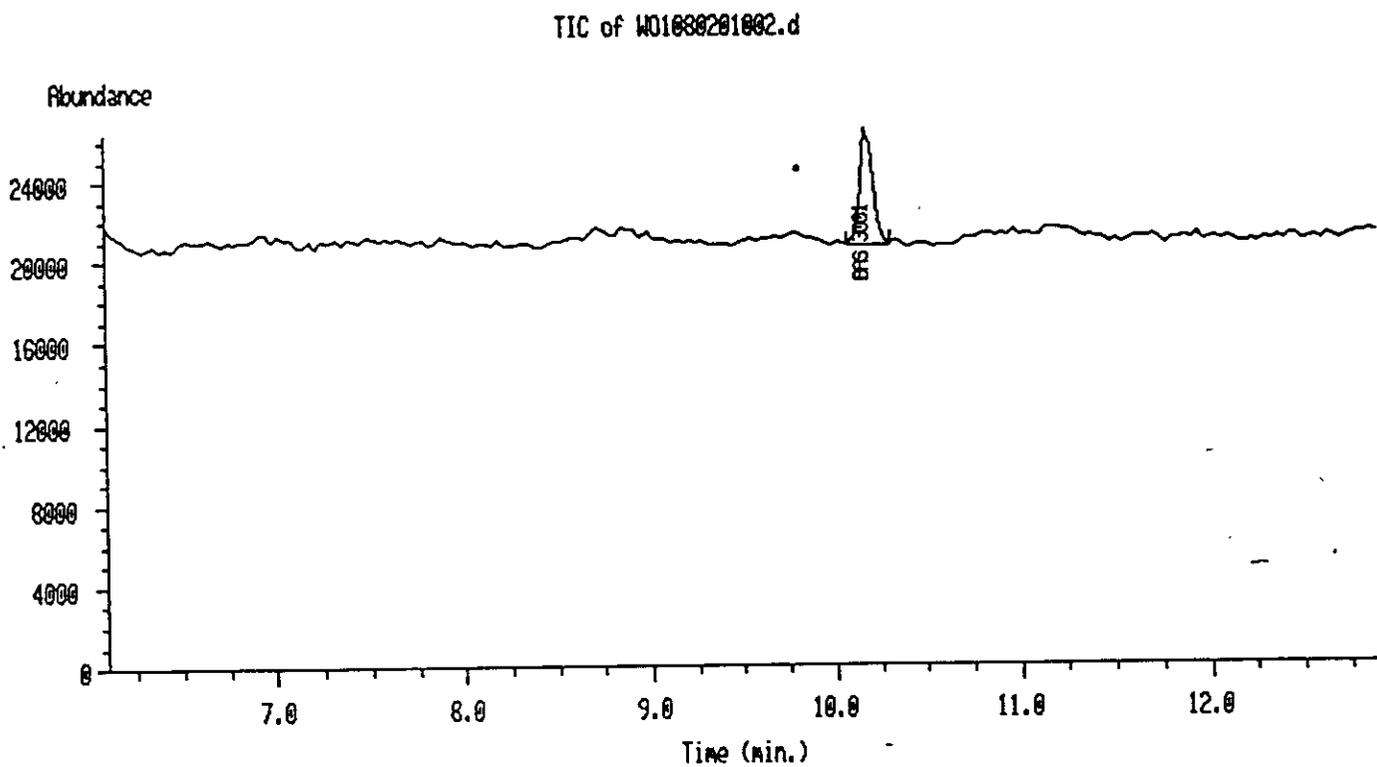


Figure 72. GC/MS chromatogram of a control whole orange sample. (Analyzed by the alternative procedure.) Master Sheet 93102-24, Sample Number 3.

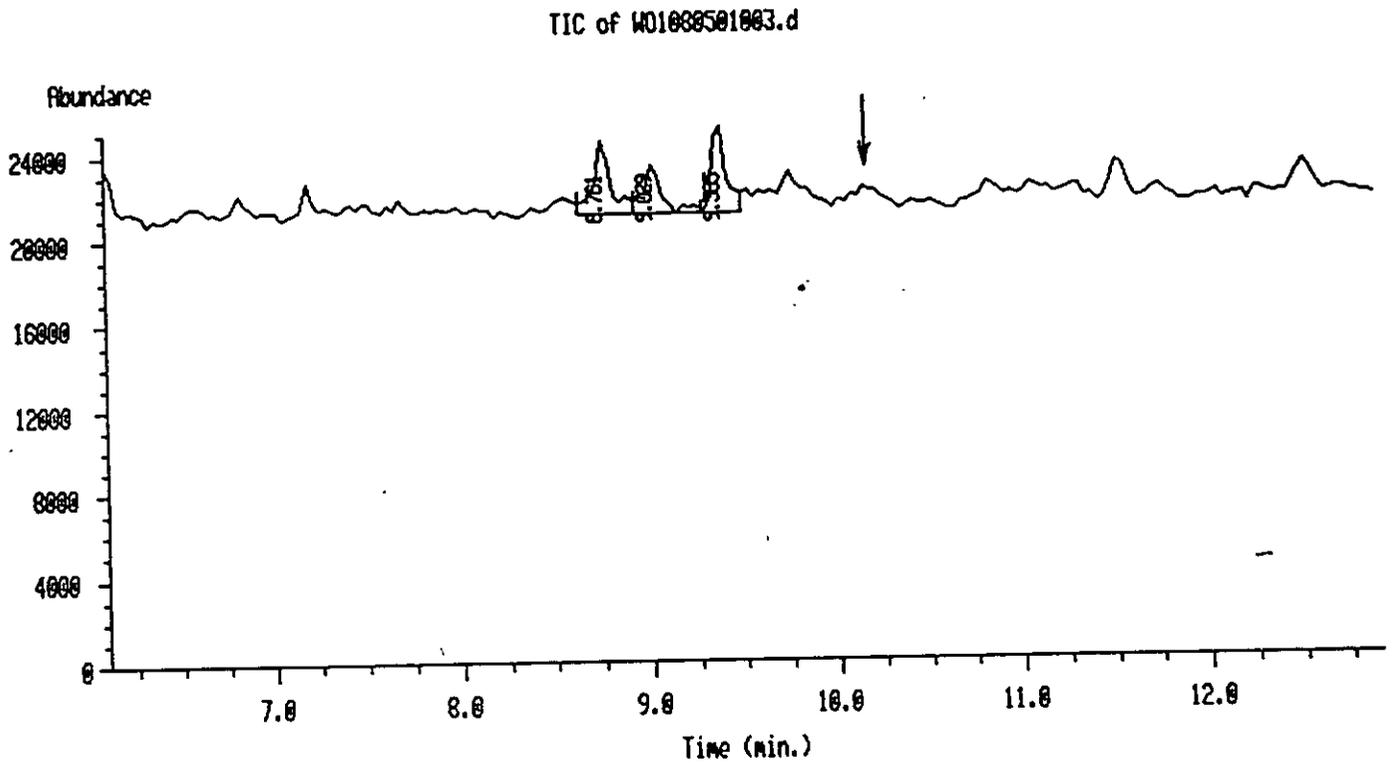


Figure 73. GC/MS chromatogram of a control whole orange sample fortified with 0.05 ppm (the quantitation limit) of BAS 300 I. (Analyzed by the alternative procedure.) Master Sheet 93102-24, Sample Number 8.

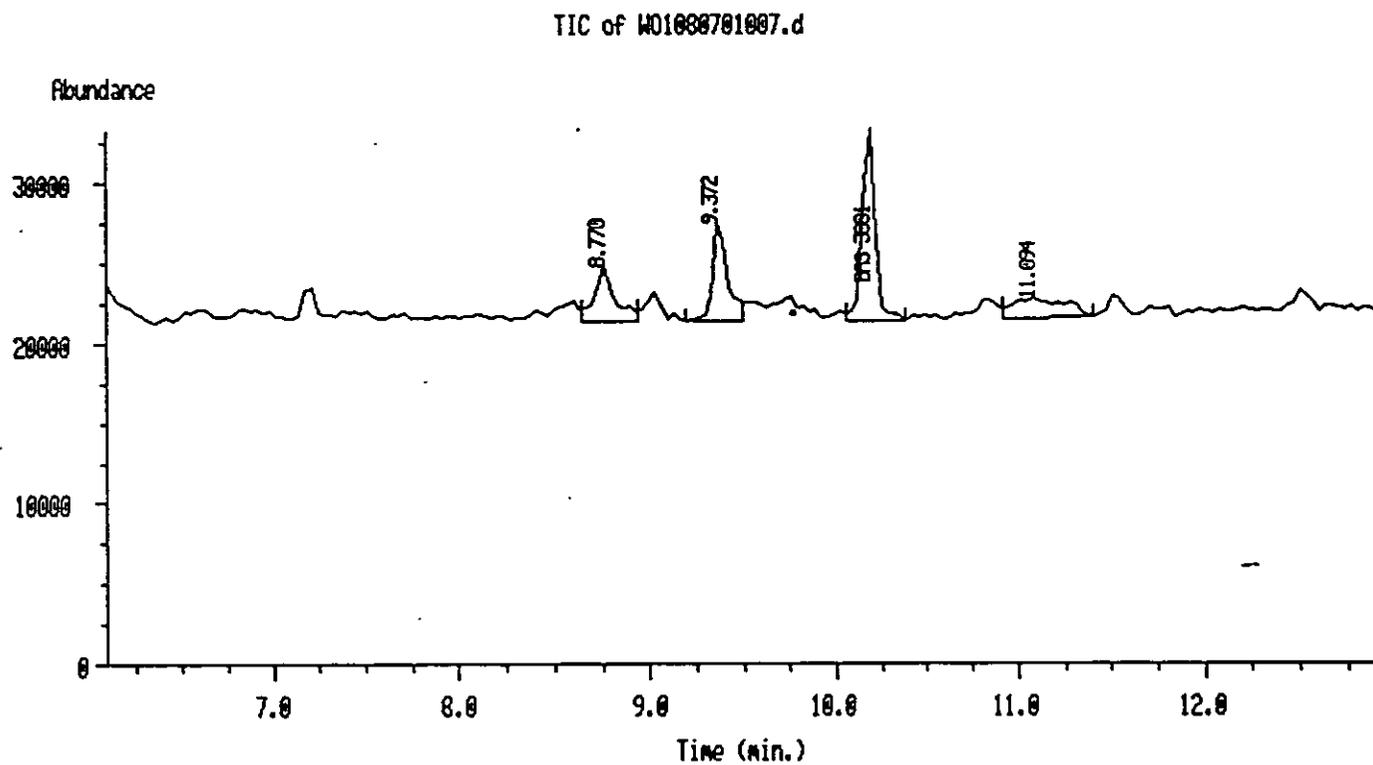


Figure 74. GC/MS chromatogram of a control whole orange sample fortified with 0.50 ppm of BAS 300 I. (Analyzed by the alternative procedure.) Master Sheet 93102-24, Sample Number 10.

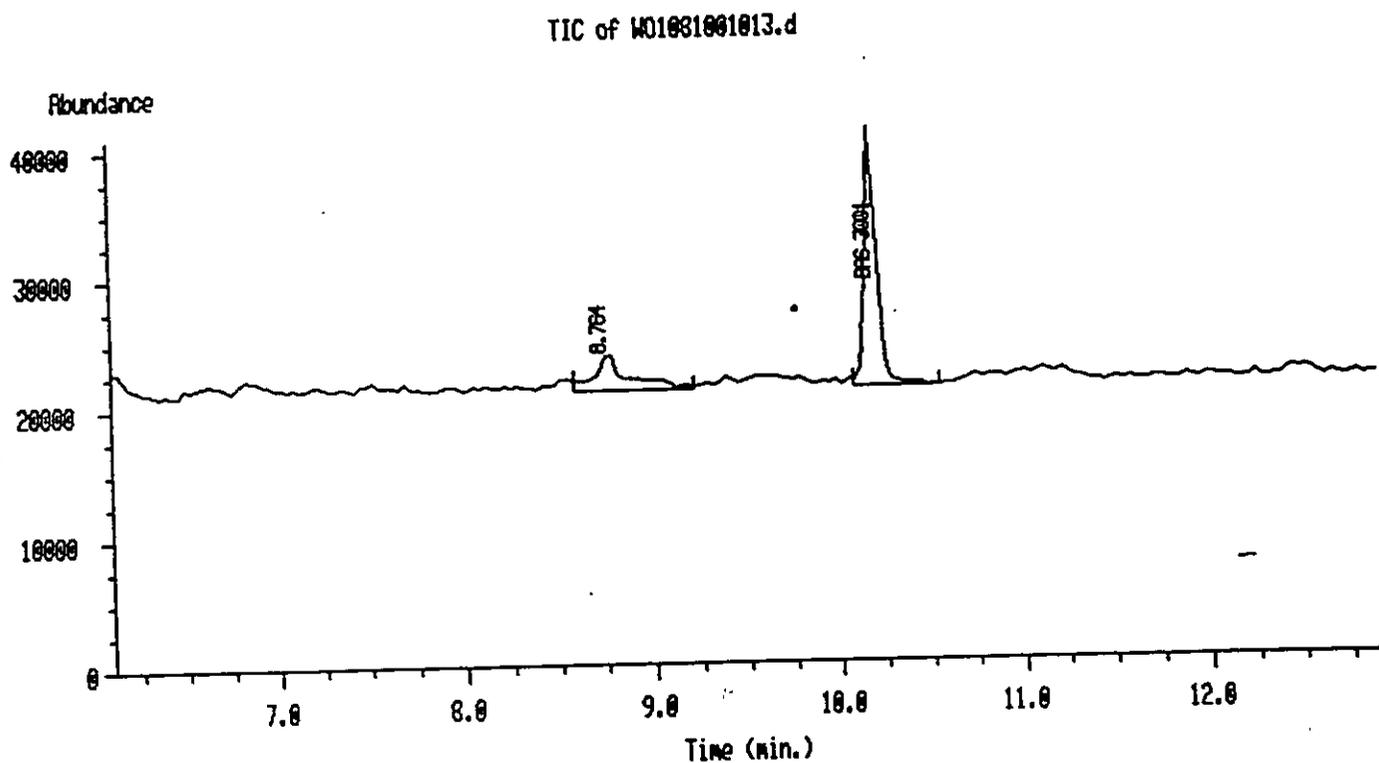


Figure 75. GC/MS chromatogram of a control whole orange sample fortified with 5.0 ppm of BAS 300 I. (Analyzed by the alternative procedure.) Master Sheet 93102-24, Sample Number 15.

