Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Quinclorac

MRID #: 410635-70

Matrix: Water

Analysis: GC/ECD

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410635-70

Study Title

Gas chromatographic determination of 3,7-dichloro-8-quinoline carboxylic acid (quinclorac) in drinking water. Method 245

Data Requirements

EPA Guideline Number: 164-2

Author

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Study Completed On

October, 1985

Performing Laboratory

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Limbergerhof, W. Germany

Registration Document No. BASF:

85/0488

This report consists of 21 pages.

33-1061

Quinclorac

EPA

MRID NUMBER

41063520

PR 86-5 DATA CONFIDENTIALITY CLAIM

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

Company BASF CORPORATION
Agricultural Chemicals Group

Company Agent: Jack R. Graham 2/28/89
Jack R. Graham Date
Manager, Registration

85/0480 0002

PR 86-5 GOOD LABORATORY PRACTICE CERTIFICATION

This study is not required to meet the requirements for 40 CFR 160, Good Laboratory Practice Standards.

Company BASF CORPORATION
Agricultural Chemicals Group

Company Agent Jack R. Graham 2/28/89
Jack R. Graham Date
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BASF AKTIENGESELLSCHAFT
LIMBUGERGERHOF AGRICULTURAL RESEARCH STATION

APE/RU
Environmental Research

October 1985
Method 245

Dr. F. Mayer

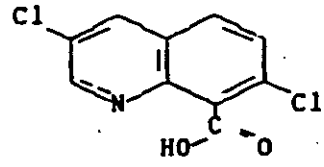
Quinclorac	Gas chromatographical determination
Drinking water	

ALL POSITIVE RESULTS OBTAINED WITH THIS METHOD HAVE IN ANY CASE TO BE VERIFIED BY MASS SPECTROMETRY, SINCE IN THIS ULTRA TRACE RANGE CONTRIBUTIONS FROM DIFFERENT INTERFERING SUBSTANCES HAVE TO BE CONSIDERED. SPECIAL CARE SHOULD BE TAKEN TO AVOID CONTAMINATION IN THE ANALYZING LABORATORY ESPECIALLY WHEN THE INVESTIGATED COMPOUNDS ARE OR WERE USED THERE.

1. INTRODUCTION

Chemical name: 3,7-dichloro-8-quinoline carboxylic acid

Structural formula:



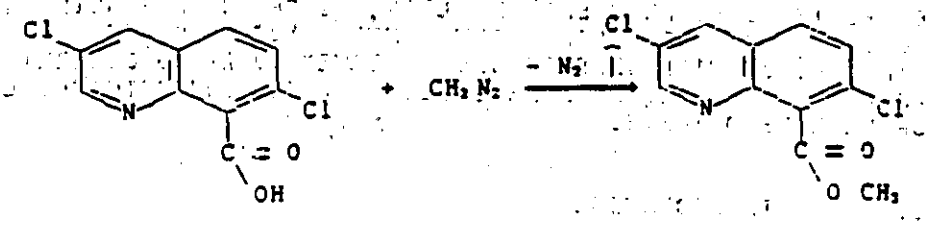
Molecular formula: $C_{10}H_5Cl_2NO_2$

Molecular weight: 242.05

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

Solvent:		
	water	6.2×10^{-3}
	acetone	0.2
	acetonitrile	<0.1
	methylenechloride	<0.1
	ethanol	0.2
	n-hexane	<0.1

Derivatization reaction for the GC determination:



2. DESCRIPTION OF THE METHOD

The active ingredient is absorbed from the water on C_{18}- alkylated silica gel, purified on a precoated silica gel column, methylated with diazomethane and determined by gas chromatography using a capillary column and an electron capture detector (^{63}Ni-ECD).

3. EQUIPMENT

Gilson-minipuls 2 peristaltic pump (Abimed Analysentechnik GmbH, Ludwigshafener Str. 26, 4000 Düsseldorf, FRG)
PH meter (WTW-Werkstätten, D-8120 Weilheim)
Graduated flasks, 100 ml
Full pipettes, 1, 2, 5 and 10 ml
Measuring cylinders, 500 ml
Flasks, 10 ml NS 10/19 (see Annex I for sketch)
Erlenmeyer flasks, 500 ml
Rapid evaporator according to Rettenberger (N-EVAP; Labotec, Wiesbaden, Gebr. Rettberg, Rudolf-Diesel-Str. 19, 3400 Göttingen, FRG)

Accessory equipment for column clean-up

Baker-10 extraction system (No. 70 18-0) with empty reservoir
Adapter (Order No. 7122-0, Baker, Gross-Gerau)
Collective rack for 10 ml flasks
Gas chromatograph:
e.g. Perkin Elmer F22 with ^{63}Ni-ECD

4. REAGENTS

Hexane, dist.
Acetone, dist.
Dichloromehtane, dist.
Methanol, dist.
H_2SO_4 1 M
One-way separating columns, silica gel Si (Baker, Order No. 70 86-3)
BONDED-PHASE-Octadecyl C 18 (Baker, Order No. 70 31-0)
Empty columns, 3 ml (Baker, Order No. 71 21-3)

Instructions for preparing diazomethane

The following amounts of reagents are required for the preparation of approx. 100 ml ethereal, about 1.5% diazomethane solution in a distillation apparatus with a descending condenser and a dropping funnel: 3 g KOH, dissolved in 5 ml water, diluted with 45 ml methanol, 6 g N-methyl-N-nitroso-P-toluene sulfonamide (diactin) dissolved in 100 ml ether.

3 g KOH dissolved in 50 ml of 90% methanol in the reaction vessel are connected to the apparatus. The receiver vessel cooled with ice and water and filled with 10 ml ether is connected to the descending condenser. 6 g diactin, dissolved in 100 ml ether, are filled into the 250-ml dropping funnel and slowly introduced dropwise into the solution of KOH in water and methanol maintained at 60°C. The whole amount of diactin solution is to be dripped in during about 30 minutes. The mixture of ether and diazomethane is to be distilled off at the same rate in order to avoid an over-concentration of diazomethane in the reaction mixture. Finally, a further 10 ml ether are added via the dropping funnel and distilled off with the remaining diazomethane. Rubber or Latex gloves must always be worn when diactin and diazomethane are being handled.

Standard solutions for additional tests

Quinclorac > 99.5% (Dr. Ohnsorge, BASF AG; APE/RU)

Prepare 100 µg/ml in acetone; dilute 1 µg/ml and 10 ng/ml with water

Standard solutions for gas chromatography

3,7-Dichloro-8-quinoline carboxylic acid methyl ester > 99.5% (Dr. Ohnsorge, BASF AG, APE/RU)
100 µg/ml; 1 µg/ml; 10 ng/ml in acetone.

3-Ethyl-7-chloro-8-quinoline carboxylic acid (internal standard) > 99.5% (Dr. Ohnsorge, BASF AG, APE/RU)
500 µg/ml; 5 µg/ml; 50 ng/ml in acetone.

In order to obtain comparable signal levels, the concentration of the internal standard must be five times as great as that of the active ingredient derivative.

STABILITY OF THE STANDARD SOLUTIONS

Storage Days	At room temperature in the light	At + 4°C in the dark
	3,7-dichloro-8-quinoline carboxylic acid 200 µg/ml in acetone	
5	100%	100%
71	100%	100%
	3,7-dichloro-8-quinoline carboxylic acid methyl ester 0.2 µg/ml in acetone + hexane = 5 + 95	
1	100%	100%
7	100%	100%
20	100%	100%
272	100%	100%
	3-ethyl-7-chloro-8-quinoline carboxylic acid methyl ester in acetone	
17	96%	96%
36	103%	109%
52	110%	103%

Quinclorac is stable in water for 30 days at pH 5, pH 7 and pH 9 at 70°C.

5. ANALYTICAL PROCEDURE

The expressions in brackets used below refer to the symbols used in the calculation formula in 7.2. All pressure specifications are to be understood as the difference to atmospheric pressure. The method is described for one sample. However, 8 samples can be handled in parallel.

5.1. Solid phase extraction

5.1.1. Preparation of the column

1 g bonded phase octadecyl is introduced into an empty column with a fritted glass disc, the material is covered with the second fritted disc, and it is placed on a Luer fitting on the cover of the extraction system. A reservoir is fixed on the column by means of an adaptor. 10 ml methanol is introduced in each case in order to wet the C_{18} material and it is sucked through the column at 20 kPa until it has reached the surface of the column packing. The methanol is displaced by 10 ml water with a pH of 2.5 (adjusted with 1 M H_2SO_4).

5.1.2. Enrichment of the active ingredient on the column

500 g water (= G) are adjusted to a pH of 2.5 with 1 M H_2SO_4 (about 1.5 ml) in a 500-ml Erlenmeyer flask and degasified for a quarter of an hour with helium. The column prepared according to 5.1.1. is connected up to the tube of the pump and placed in the water with its opening

downward. By gently shaking the tube, the air bubble between water and C_{18} material is displaced. Then 2.5 ml water/min. is drawn through the column with the peristaltic pump.

5.1.3. Prewashing of the column

The active ingredient-laden C_{18} column is replaced on the extraction system and each of the unused openings is closed with a plastic stopper. Air is sucked through the column at 40 kPa for half a minute.

4 ml of a mixture of acetone + hexane = 3 + 97 are drawn through the column by means of the reservoir. The cover of the extraction system is removed together with the columns and the stainless steel rack with the 10-ml flasks (receivers) are placed in the basin. Before the cover is put back on, small amounts of washing liquid that may be hanging on the outlets of the Luer fittings are wiped off.

5.1.4. Elution of the active ingredient

7 ml of a mixture of acetone + hexane = 25 + 75 are applied via the reservoir and sucked through the column at 20 kPa. The eluate in the 10-ml flasks is evaporated to dryness in a stream of nitrogen on the N-EVAP at 40°C. The residue in the ultrasonic bath is dissolved in 1 ml dichloromethane.

5.2. Purification of extract on silica gel

The extract from 5.1.4. is now applied to a Baker 3-ml silica gel separating column. The flask is rinsed out with 0.5 ml DCM, and the whole solution and then, for 10 sec., air at 20 kPa are sucked through the column.

Preliminary washing is carried out by drawing 4 ml methanol + DCM = 20 + 80 through the column. Then the stainless steel rack with the 10-ml flasks as receiver is placed in the basin, residues of washing liquid are wiped off the outlets and the cover with the columns is replaced. The active ingredient is eluted with 3 ml methanol + DCM = 40 + 60 (vacuum 20 kPa) and the eluate is evaporated to dryness at 40°C in a stream of nitrogen.

5.3. Methylation

The residue from 5.2. is dissolved in 0.5 ml acetone. 2 ml of ethereal diazomethane solution are added and the whole is left to stand for one hour. The solution must then still be colored yellow; otherwise a further 2 ml diazomethane solution are added and a further hour is waited. Then the solvent is blown off in a stream of nitrogen at 30°C and the residue is dissolved in 0.5 ml of a solution of the internal standard in acetone.

6. GC conditions

Equipment:	e.g. Perkin-Elmer, F 22 with ^{63}Ni-ECD
Column:	SE54, 19 m WCOT, 0.28 mm i.d., film thickness 0.5 µm
Injection volume:	1 µl
Injector:	260°C
Oven:	200°C
Detector:	370°C
Carrier gas:	He, 1000 mbar
Make-up gas:	Ar + CH_4 = 90 + 10; 30 ml/min.

7. EVALUATION

7.1. Method of evaluation

The signals are evaluated via the peak height. In the calibration curve the peak height (in counts or mm) is plotted against the weight of the injected standard.

A calibration curve is prepared by injecting at least three standard amounts. For each series of analyses two samples of water that are free of the active ingredient (blank samples) and two additional tests are subjected to the analytical procedure.

One of the blank samples is taken up in pure acetone (not in solution with the internal standard) for the GC injection. If the chromatogram

of this sample is clean at the retention time of the internal standard, the series of samples is evaluated via the internal standard. For this purpose, instead of the peak heights, the quotients of the peak heights of samples (or additional tests and calibration curve) and internal standard are used. The concentration of the internal standard in the final volume must always be the same within a series of analyses!

For the additional tests water that is free of the active ingredient is mixed with a known amount of quinclorac that is in the same order of magnitude as the expected residues. The yield factor (= F) is determined from the additional tests. The evaluation can also be carried out by means of an appropriate computer program.

7.2. Calculation of the content

The content of quinclorac (R) in µg/kg is calculated by means of the following formula:

$$R = \frac{V_E \cdot W_A \cdot F}{G \cdot V_I}$$

G = sample weight in g
V_E = final volume of the extract before injection in ml
V_I = partial volume injected from V_E in µl
F = yield factor determined by investigator through additional tests

$$F = \frac{100\%}{\text{yield in \%}}$$

W_A = amount of active ingredient derived from the calibration curve in pg

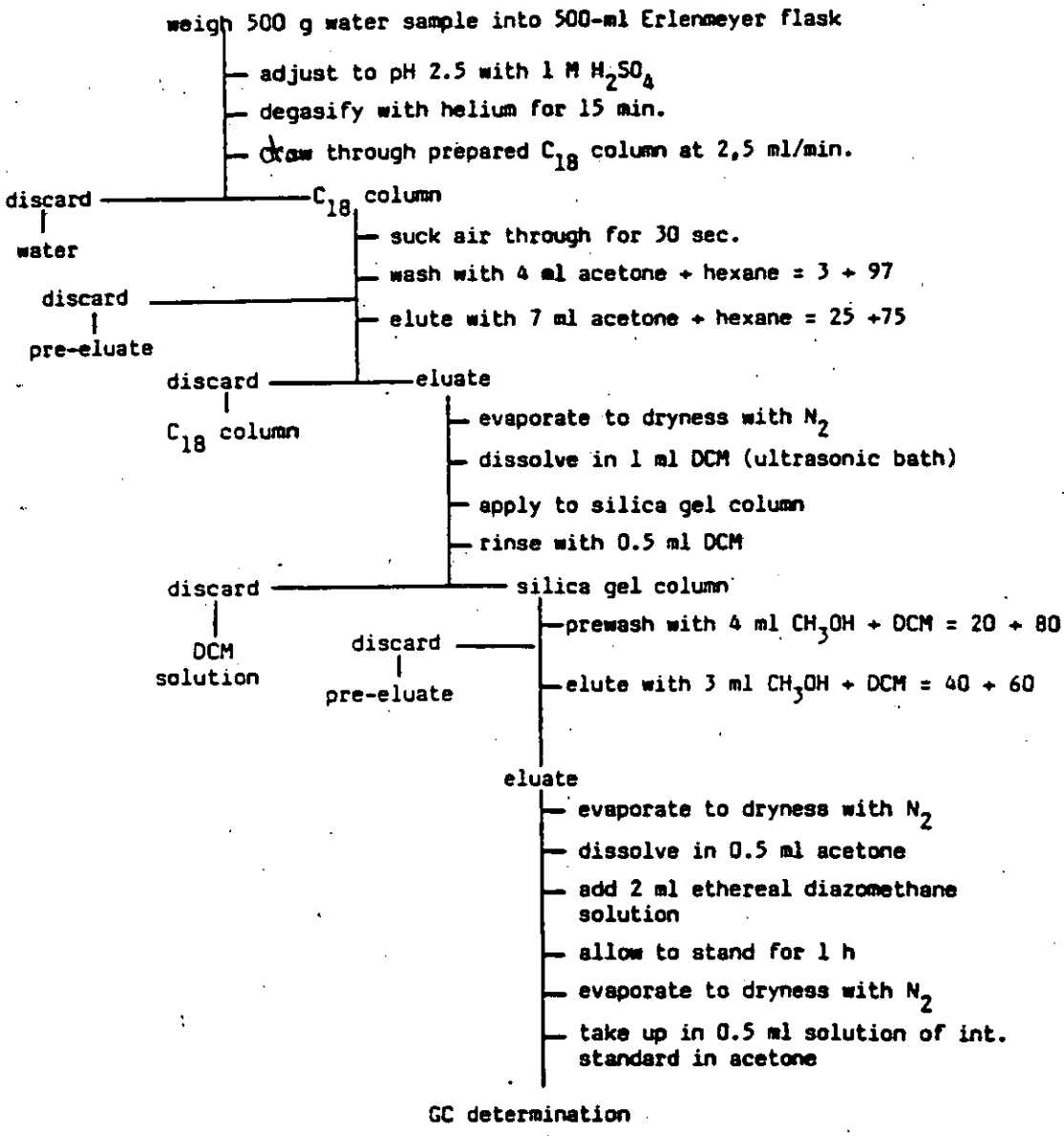
8. YIELD, REPRODUCIBILITY AND LOWEST CONCENTRATION DETERMINED

Quinclorac in drinking water

Addition of quinclorac ng/kg (ppt)	Evaluated according to standard	Yield %	Mean %	Standard deviation ±	Variation coefficient ± %
200	internal	86.5; 89.0; 82.1; 84.8; 84.3	85.34	2.58	3.02
10 *	external	84.7; 92.2; 72.8; 91.1	85.20	8.90	10.45

* limit of determination

9. ANALYTICAL SCHEME



10. REMARKS

All glass apparatus must be rinsed with acetone before being used for analyses at the limit of determination.

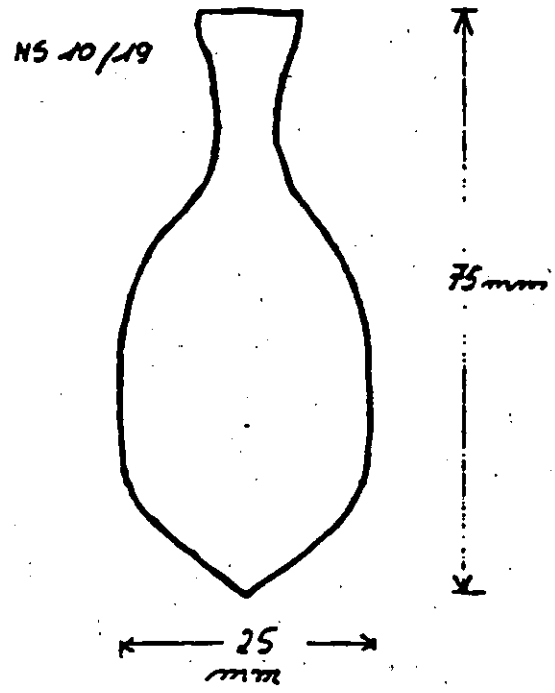
In the event that traces of C_{18} material go into solution in the elution of the active ingredient, they are removed again by the following silica gel column clean-up.

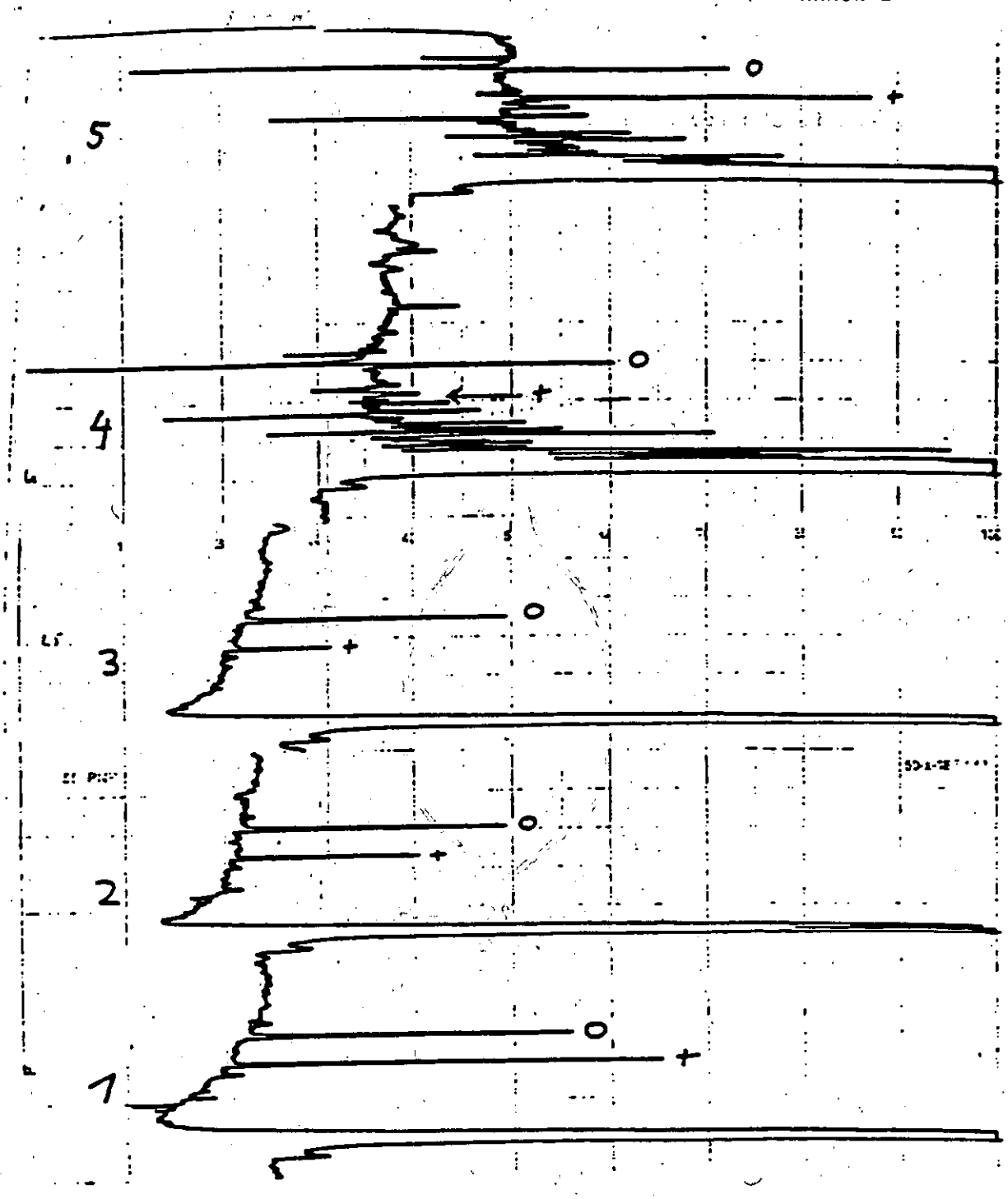
Technical procedure: H. Sträßner

Annexes

1. 20-ml flasks for Baker high-grade steel rack
2. Gas chromatograms
3. 4th calculation

10-ml flasks for Baker stainless steel rack





1: standard 10 pg
2: standard 5 pg
3: standard 2.5 pg
4: blank sample V_E = 0.5 ml, V_I = 1 µl
5: addition of ng/kg V_E = 0.5 ml, V_I = 1 µl
+: active ingredient derivative
=: internal standard; on account of the following negative peak not suitable here for evaluation

BASF Limburgerhof --- Evaluation --- Environmental Chemistry APE/RU

Queue file name	: ST85037.LST	Report number	: 02/01
Investigator	: STRAESSNER	Date of report	: 30/10/85 07:33:47
Sample material	: WATER	Method number	: 245/01/01
Culture	:	Injection volume (µl)	: 1.0
Act. ingred./metab.	: BAS514H	Detection limit (NG/kg)	: 1.0
Internal standard	:	Blank value	: ST231 .01
Derivative determ.	: QUINCLORAC M.ESTER	Derivat. factor	: 0.945
Subst. concerned	: QUINCLORAC	Conversion factor	: 1.0
Eval. accord. to	: Peak height	Mean recovery	: 82.0
Remarks	:		

Protocol	:		
Study	:		
Study section	: 0	0	0
Sample number	: ST231 .01	ST232 .01	ST233 .01
Descr. of sample	: U	Z1	Z2
Sample weight (g)	: 500.0	500.0	500.0
Aliquot (%)	: 100.0	100.0	100.0
Final dilution (ml)	: 0.5	0.5	0.5
Peak area subst.	: 2818	12600	14617
Peak height subst.	: 66	402	481
Peak area i.std.	:		
Peak height i.std.	:		
Quotient sub/i.std.	:		
Residue (µg/kg)	: < detect. limit		
Addition (NG)	:	5.0	5.0
Addition (µg/kg)	:	0.0100	0.0100
Recovery (%)	:	72.8	91.1

BASF Limburgerhof --- Evaluation --- Environmental Chemistry APE/RU

Queue file name	: ST85037.LST	Report number	: 03/01
Investigator	: STRAESSNER	Date of report	: 29/10/85 13:52:04
Sample material	: WATER	Method number	: 245/01/01
Culture	:	Injection volume (µl)	: 1.0
Act. ingred./metab.	: BAS514H	Detection limit (NG/kg)	: 1.0
Internal standard	:	Blank value	: ST231 .01
Derivative determ.	: QUINCLORAC M.ESTER	Derivat. factor	: 0.945
Subst. concerned	: QUINCLORAC	Conversion factor	: 1.0
Eval. accord. to	: Peak height	Mean recovery	: 88.5
Remarks	:		

Values identified with * lie outside the calibration series

Protocol	:			
Study	:			
Study section	:	0	0	0
Sample number	:	ST231 .01	ST236 .01	ST237 .01
Descr. of sample	:	U	Z3	Z4
Sample weight (g)	:	500.0	500.0	500.0
Aliquot (%)	:	100.0	100.0	100.0
Final dilution (ml)	:	0.5	0.5	0.5
Peak area subst.	:	2818	14997	18312*
Peak height subst.	:	66	507	546*
Peak area i.std.	:			
Peak height i.std.	:			
Quotient sub/i.std.	:			
Residue (µg/kg)	:	< detect. limit		
Addition (NG)	:		5.0	5.0
Addition (µg/kg)	:		0.0100	0.0100
Recovery (%)	:		84.7	92.2*