

US EPA ARCHIVE DOCUMENT



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

PMSD 0856

JUN 20 1986

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

Ms. Alice Marcotte
Technical Editing Group (HFF-40)
Food and Drug Administration
200 C Street SW.
Washington, DC 20204

Dear Alice,

Enclosed are materials for updating one old entry in PAM-II.

The chemical is: Trifluralin 40 CFR 180.207. This method is presently in PAM-II as Method A. The Registration Standard for Trifluralin noted the method should be validated as an enforcement procedure, thus it should become Method III. We are sending this material to you because this is an improvement in the trifluralin methodology, and the method is applicable to other vegetable crops with established tolerances.

If there are any questions about this material, please contact me at 557-0486.

Sincerely,

Dick

Francis D. Griffith, Jr.
Residue Chemistry Branch
Hazard Evaluation Division (TS-769C)

Attachments: I - PAM II Cover Sheet
II - Method Trial Report Evaluation by RCB
III - Method Trial Report from ACL/COB/BUD
IV - Method Trial Request

cc: (FDA letter all Attachments) M. Bradley

→ cc: (FDA letter plus Attachments I-III) T. Murtagh (ISS/ISB/PMSD)

Attachment I

Acceptable Name: Trifluralin

Pesticide Reg. 40 CFR 180.207

Structure: See Original Entry

Other Names: Triflan, Ipersan, Digermin, Triflurex

Petitioner: Elanco Products Company, Division of Eli Lilly
and Company Indianapolis, IN 46285

Method III

Pesticide Petition: -

Product Application: Carrots, Green Beans, Brassica Vegetables

Detection Limit: <0.01 ppm

Method Trial Report: See Attachment #3; EPA Comments 1 and 2

Notes: See Attachment #3 page 2

Special Reference: PAM-II Trifluralin Method A now becomes
PAM-II Trifluralin Method III

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

JUN 13 1986

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Registration Standard for Trifluralin
Method Tryout Report Evaluation
(No Accession No.) [No RCB No.]

FROM: Francis D. Griffith, Jr., Chemist
Residue Chemistry Branch
Hazard Evaluation Division (TS-769C)

TO: Richard F. Mountfort (PM-12)
Fungicide-Herbicide Branch
Registration Division (TS-769C)

THRU: Charles L. Trichilo, Chief
Residue Chemistry Branch
Hazard Evaluation Division (TS-769C)

Residue Chemistry Branch (RCB) has been informed by Analytical Chemistry Laboratory (ACL), Chemical Operations Branch (COB), Benefits and Use Division (BUD) of the completion of the requested trifluralin method trial. The method trial for trifluralin residues was reported by King T. Zee in his memo dated May 5, 1986.

The method trial was requested for trifluralin (a,a,a-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) on carrots, green beans, and a Brassica vegetable (see memo by F.D. Griffith, Jr., dated August 21, 1985 to COB/BUD). The method trial was requested for the Eli Lilly and Company procedure No. 5801110 listed as Method A in the Pesticide Analytical Manual Vol-II (PAM-II) and titled "Determination of Trifluralin Residues in Agronomic Crops When the Pesticides BHC, Ethion and/or Zineb are Present in the Crop Sample." The method tryout was initiated to overcome a deficiency noted in the Trifluralin Registration Standard (see pg 21 of the Standard). The method had a data of October 15, 1964, but no author(s) was listed on the cover page.

The method trial to recover trifluralin was conducted using the PAM-II Method A procedure with minor modification as noted on page two of the method trial report memo (op. cit.). No corrections were made for unspiked crop samples; ACL has determined the trifluralin limit of detection (L.D.) in carrots, green beans, and Brassica vegetables is less than 0.01 ppm.

RCB requested the method be validated for trifluralin residues in carrots at 1.0 ppm, in green beans and Brassica vegetables at 0.05 ppm. In addition to revalidating the method at the established tolerance, each of the commodities was spiked with the added mixture of 1 ppm BHC, 7 ppm zineb, and 1 ppm ethion to ascertain the ability of the TLC cleanup step to remove these potential interferences. Without the added mixture the recovery of trifluralin from carrots was 105%, from green bean at 85% and from brassica vegetables at 78%. RCB concludes these data revalidate the original MTO (see memo PP#7F0514, J. Wolff 6/14/67). When the mixture was added to carrots the trifluralin recoveries ranged from 113% to 115% ($\bar{X} = 113\%$, $n = 2$). When the mixture was added to the 0.05 ppm trifluralin spike in green beans the trifluralin recoveries ranged from 72% to 77% ($\bar{X} = 74.5\%$, $n = 2$). Likewise when the mixture was added to a 0.05 ppm trifluralin spiked Brassica vegetable trifluralin recovery was 70% ($n = 2$). It was not our intent to have recovery data for any pesticide in the added mixture. It was our intent to be certain if any of these pesticides were present along with trifluralin residues we could accurately enforce the trifluralin tolerances. RCB concludes a successful method tryout has been completed. This method is suitable to gather trifluralin residue data and enforce trifluralin tolerances in the presence of interfering pesticide; i.e., BHC, ethion, and zineb.

The analytical standard for trifluralin is available from EPA's Pesticide and Industrial Chemicals Repository Research Triangle Park, NC (code number for trifluralin is 6800). Likewise standards for zineb (code 7120), ethion (code 3340) and BHC, mixed isomers, technical (code 0600) are also available from the Repository.

ACL/COB noted the TLC cleanup step did not completely separate BHC, ethion, and/or zineb residues from trifluralin residues. ALC's supporting GC chromatographic data using a 5% SE-30 column shows effective and quantitative separation of trifluralin residues from these pesticides. RCB concurs the GC step shows separation, and will have ACL's two comments printed when the method is reprinted in PAM-II with a Roman numeral designation.

ALC reported four samples can be analyzed within two working days. RCB concludes this time factor is acceptable for regulatory purposes.

RCB Conclusions:

1. There has been a successful method tryout for recovery of trifluralin residues in carrots, green beans, and Brassica vegetables with the interfering pesticides BHC, ethion, and zineb present. The method with EPA comments is suitable to gather residue data and enforce tolerances.
2. The deficiency noted in the Trifluralin Registration Standard and RCB's MTO request has been resolved.

RCB Recommendation

The analytical method for trifluralin presently published in PAM-II as method A should be republished in PAM-II as method III along with the EPA comments.

TS-769C:RCB:Reviewer(FDG):vg:CM#2:Rm708:577-0486:6/11/86:edited:fdg:6/13/86
cc: R. F. Circu., Reviewer, PMSD/ISB, M. Bradley, D. Marlow (COB/BUD),
Registration Standard File for Trifluralin, R. F. Thompson (RTP-NC)
RDI: R. D. Schmitt: 6/6/86: R. S. Quick: 6/6/86



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
 WASHINGTON, D.C. 20460
 Analytical Chemistry Section
 Building 402, ARC-East
 Beltsville, Maryland 20705

Rec'd 5/1/82

OFFICE OF
 PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM:

SUBJECT: Registration Standard for Trifluralin. Method Trial Request

FROM: King T. Zee, Chemist *King T. Zee*
 Analytical Chemistry Laboratory

THRU: Warren R. Bontoyan, Head *WAB*
 Analytical Chemistry Section

THRU: Donald A. Marlow, Chief *DM*
 Chemical Operations Branch

TO: Charles Trichilo, Chief
 Residue Chemistry Branch
 HED

A method trial was requested by Residue Chemistry Branch, HED, for Trifluralin on carrots, Brassica Vegetable, and green beans. PAM II, general procedures 5801210 and 5801110 is to be used for the analysis. Method 5801210 entitled Crops "Determination of Trifluralin Residues in Agricultural and Method 5801110 entitled "Determination of Trifluralin Residues in Agronomic Crops when the Pesticides BHC, Ethion and/or Zineb are Present in the Crop Sample" were developed by Eli Lilly & Co.

Procedure no. 5801210 was apparently subjected to a successful method trial 6/14/67, but procedure 5801110 (PAM vol. II, Sec. 180207), which is the preferred regulatory method, has apparently not been subjected to an FDA/EPA method tryout.

We have successfully tried the method 5801110. Interfering chemicals were separated on the silica TLC step described in the 5801110 method.

Instrument: H.P 5840 A & Integrator
 Column: 6x1/4 5% SE 30 m Chromosorb w HP 60/80
 oven : 200°C
 : 250°C
 F.C Detector: 250°C

Trifluralin has 4.2 minute retention time and 0.5 ng give 60% FSD at attenuation 7.

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Results: All controls are <0.01 ppm

	<u>Chemical fortified</u>	<u>Added (mixture)</u>	<u>% Recovery</u>
		1 ppm BHC 7 ppm zineb 1 ppm ethion	
Carrots	1.0 Trifluralin	mixture not added	105
		mixture added	115 111
Brassica	0.05 Trifluralin	mixture not added	78
		mixture added	70 70
Green bean	0.05 Trifuralin	mixture not added	85
		mixture added	77 72

Comment

In our trial of the method there was evidence of presence of BHC and/or Ethion in our GC chromatograms. Both BHC and Ethion have 5.74-5.76 minutes retention time. Trifluralin has a 4.31 minute retention time; therefore, the chromatograms are judged to be satisfactory.

It seems that TLC does not completely separate BHC, Ethion and Zineb from Trifluralin, but the 5% SE 30 GC column is effective in the separating Trifluralin. The method is acceptable for enforcement analysis. It takes two days to analyze 4 samples.

USE SEPARATE FORM FOR EACH METHOD

Modifications to method (major or minor): None

Special precautions to be taken: None

Source of analytical reference standards: RTP and ACS

If derivitized standard used, give source: None

Instrumentation for quantitation: HP 5840A - GC-EC

Instrumentation for confirmation: None

If instrument parameters differ from method given, list parameters used: See report

Commercial source for any special chemicals or apparatus: None

Comments: BHC, Zineb and Ethion do not interfere with Trifluralin Method.

Chromatograms: Included

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Method: (Report No. and/or title, date) USE SEPARATE FORM FOR EACH METHOD

Do not use control values for recovery corrections.

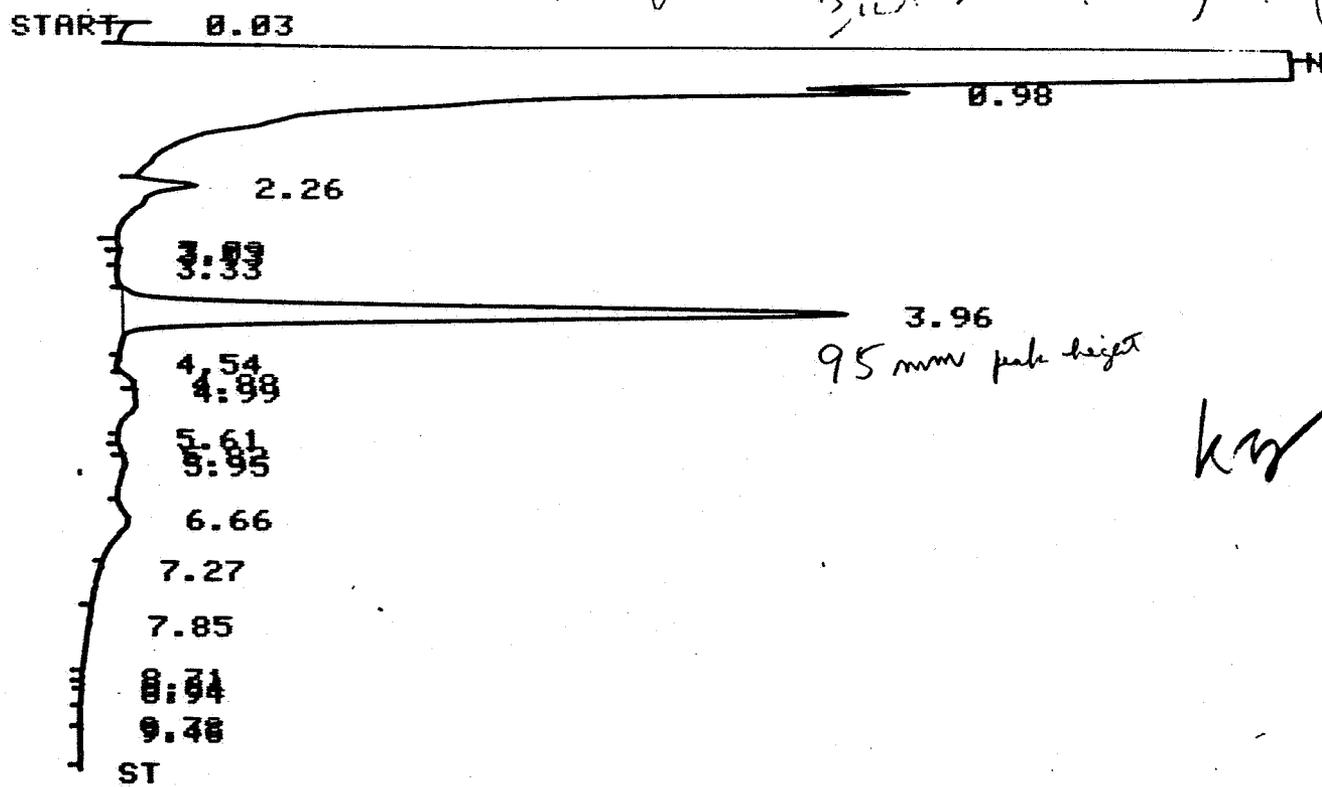
Do not report control values as 0; if less than limit of detection, report as such.

<u>Commodity</u>	<u>Chemical added</u>	<u>PPM added</u>	<u>PPM found</u>	<u>% Recovery</u>
Carrots*	Trifluralin	1 ppm	105	105
	BHC	1		
	Zineb	7		
	Ethion	1		
	Trifluralin	1	1.15 1.11	115 111
Brassicia*	Trifluralin	0.05	0.039	78
	BHC	1		
	Zineb	7		
	Ethion	1		
	Trifluralin	0.05	0.035 0.035	70 70
Green beans*	Trifluralin	0.05	0.0425	85
	BHC	1		
	Zineb	7		
	Ethion	1		
	Trifluralin	0.05	0.036 0.038	72 76

* All controls are <0.01 ppm

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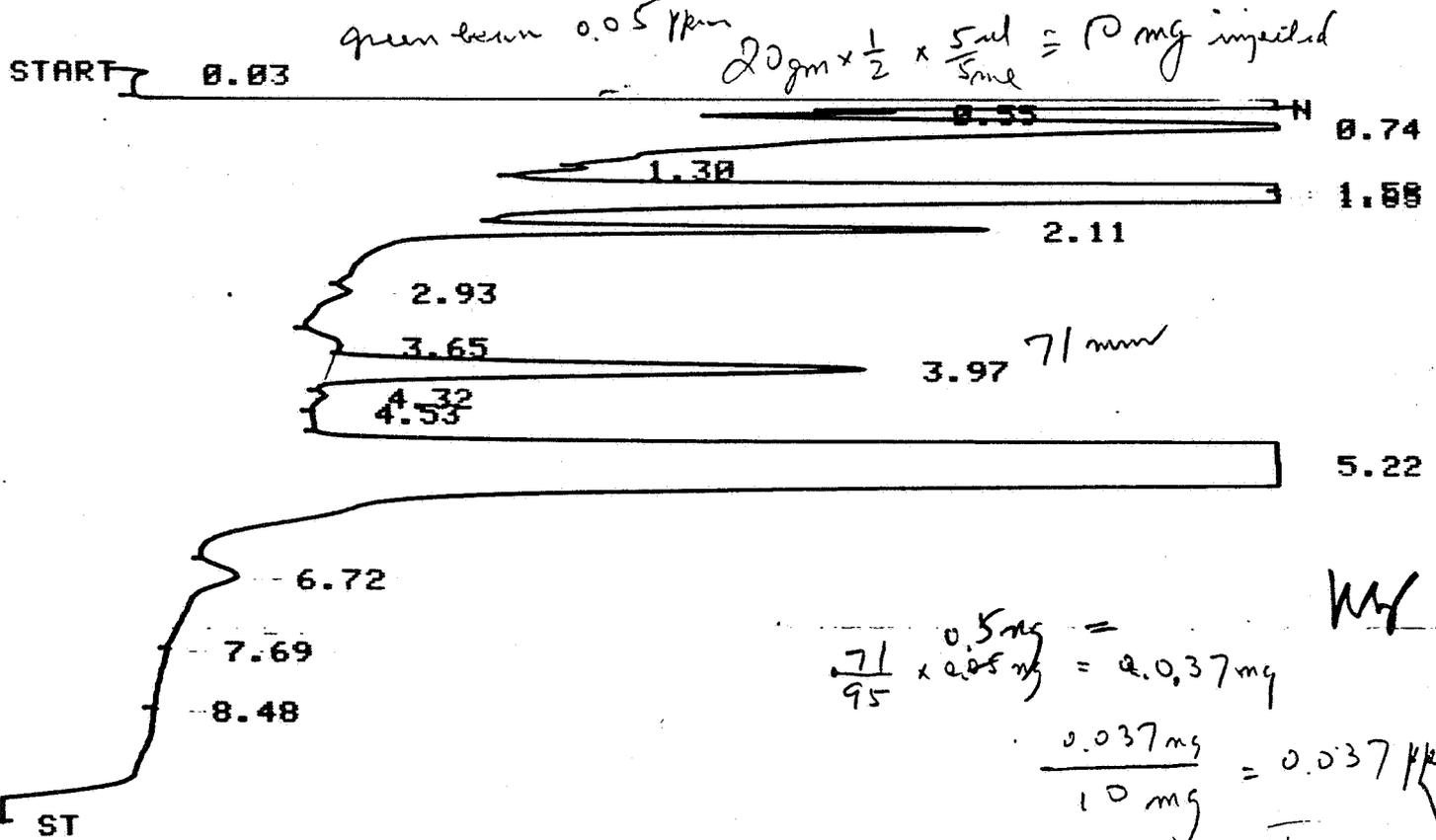
0.1 mg Trifluoromethyl $S_{\text{inj}} \approx 0.5 \text{ mg Trifluoromethyl}$



HP RUN # 255
ESTD

RT	EXP RT	AREA	CAL #	AMT
4.99	4.81	10380	(R) 1	0.016

DIL FACTOR: 1.0000 E+ 0



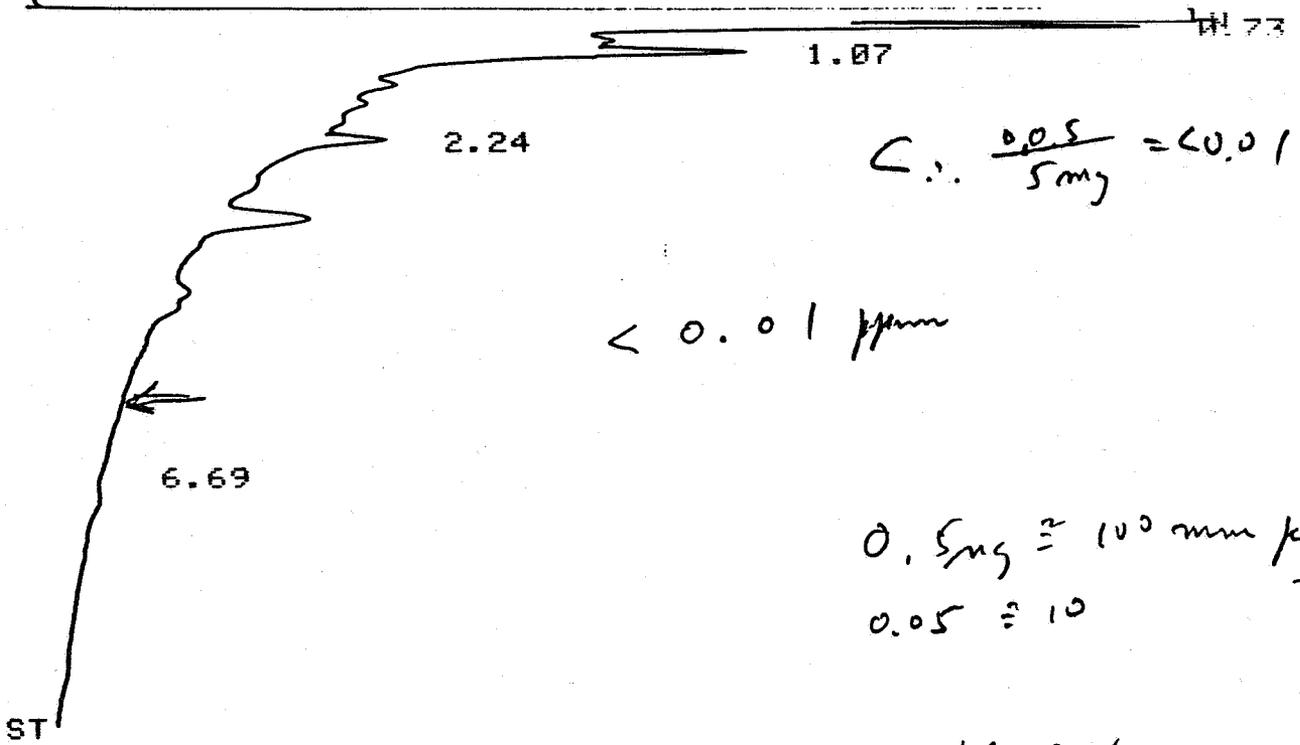
HP RUN # 256

$20 \text{ gm} \times \frac{1}{2} \times \frac{5 \text{ ml}}{5 \text{ ml}} = 10 \text{ mg injected}$
 $\frac{71}{95} \times 0.5 \text{ mg} = 0.037 \text{ mg}$
 $\frac{0.037 \text{ mg}}{10 \text{ mg}} = 0.037 \text{ ppm}$
 $\approx 74\%$

DIL FACTOR: 1.0000 E+ 0

Cont. C 20gm x 5/20ml = 5mg. Carried to inj, after floccal column cleanup

START 0.04

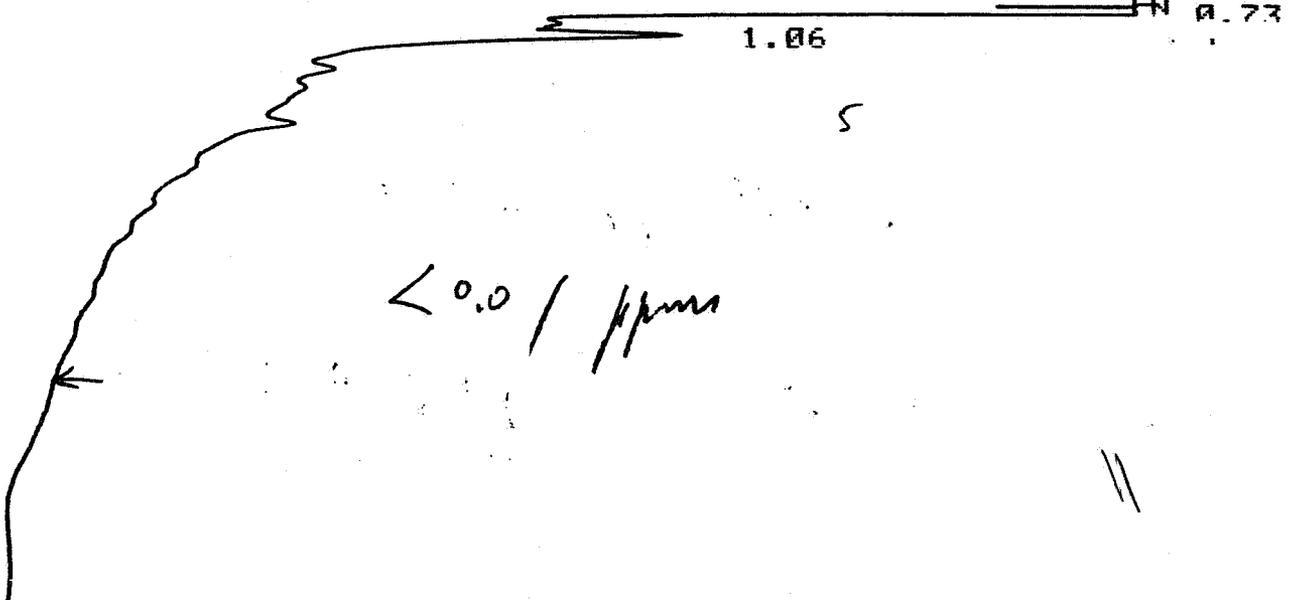


HP RUN # 9
AREA %

RT	AREA	AREA %
0.04	877	0.008
0.52	10330000	89.752
0.73	110600	0.961
1.07	434500	3.775
2.24	633500	5.504

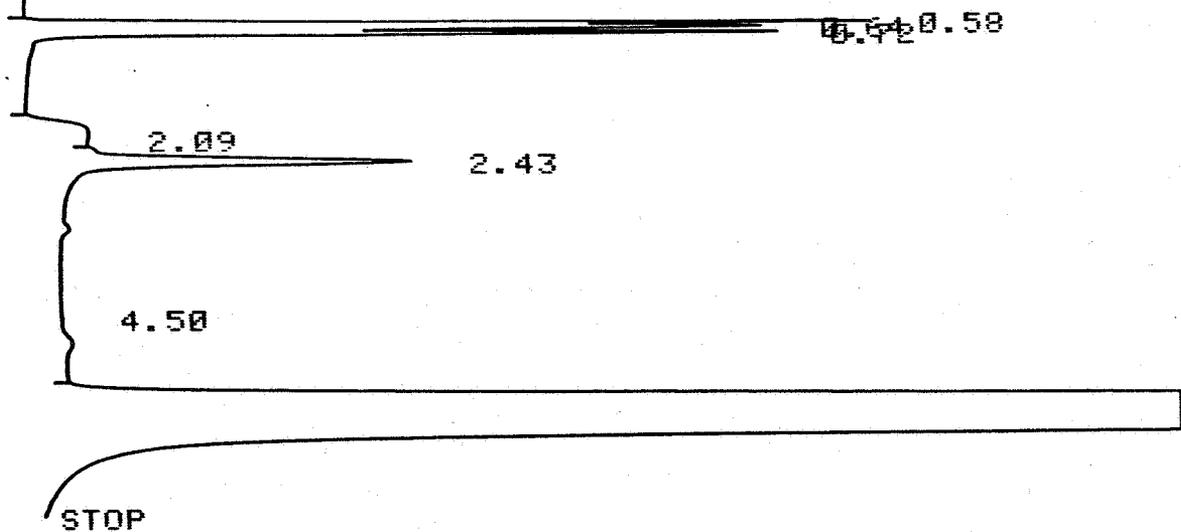
DIL FACTOR: 1.0000 E+ 0

START 0.05 ② 20gm Carri's control, $\frac{5}{20ml} = 5mg \text{ inj}$



START 21 9 0

DIL ↓

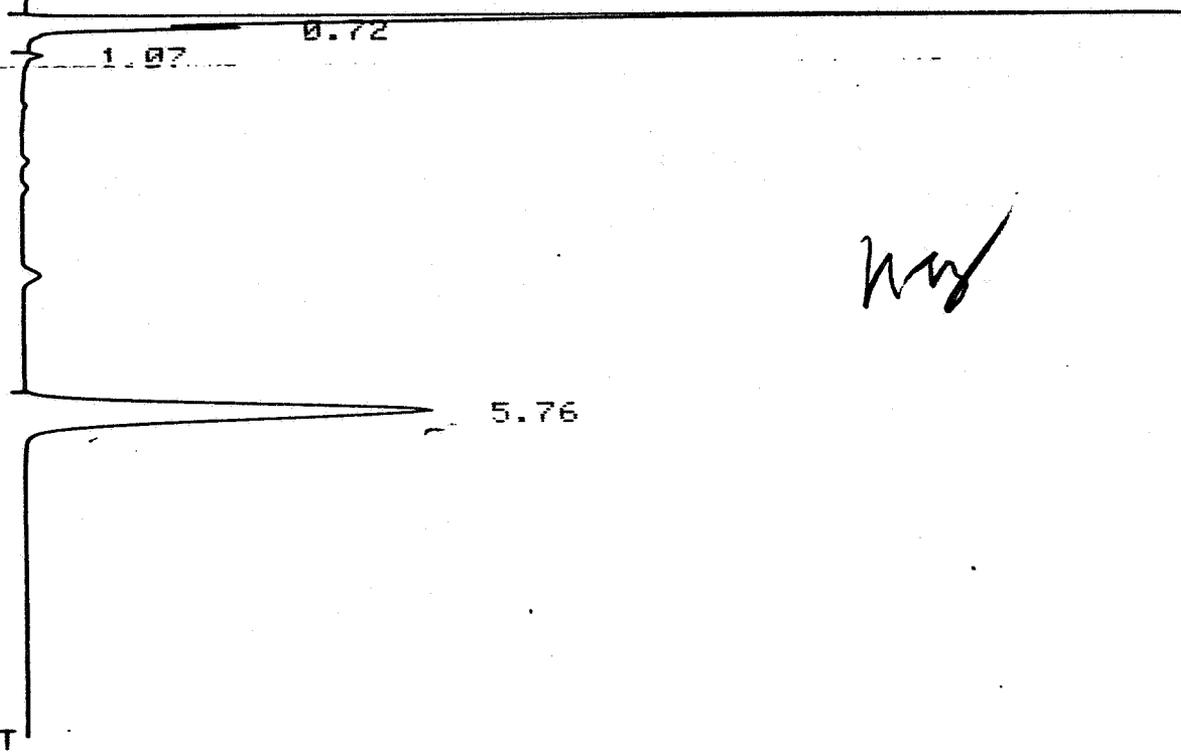


5:54
B-11

HP RUN # 50
AREA %

ESCAPE
START

Elution ↓



0.58

hw

HP RUN # 51
AREA %

RT	AREA	AREA %
0.58	258200	37.984
0.72	44700	6.576
1.07	3367	0.495
5.76	373500	54.945

DIL FACTOR: 1.0000 E+ 0

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DELETE STOP
START

Elution

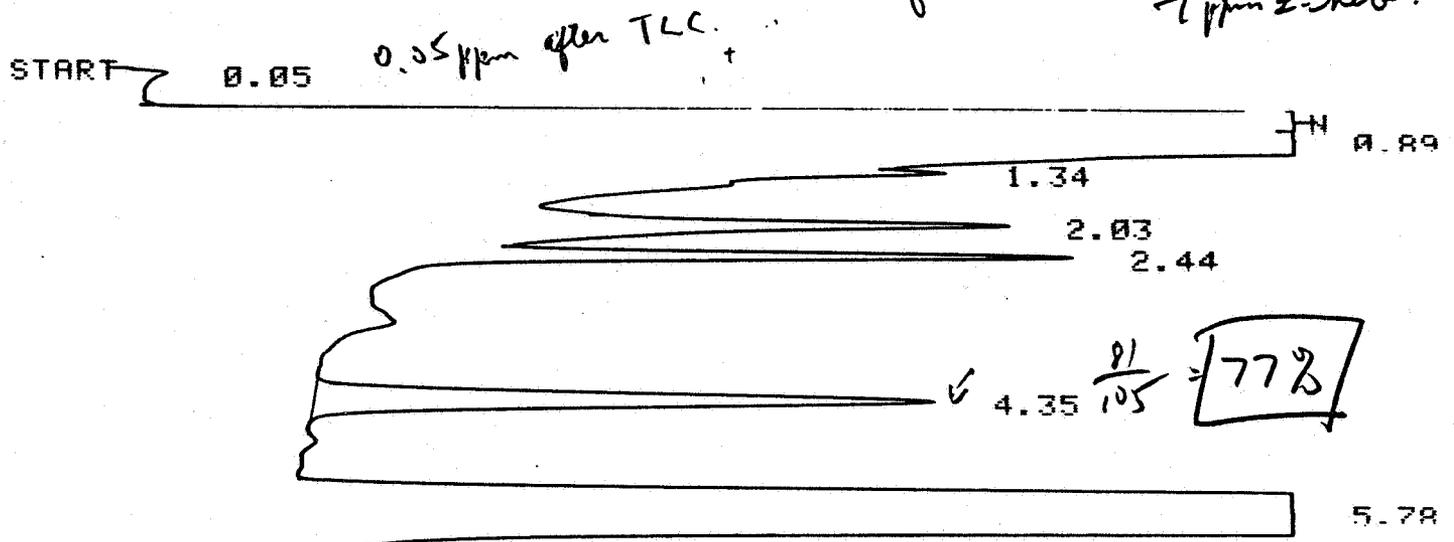
ST

HP RUN # 48
AREA %

RT	AREA	AREA %
0.05	1762	0.011
0.53	9598000	61.101
0.89	523800	3.335
1.35	205700	1.309
2.02	208200	1.325
2.43	333000	2.120
4.31	202900	1.292
5.74	4635000	29.507

DIL FACTOR: 1.0000 E+ 0

Beans fortified with 1 ppm BHC, Ethion & 7 ppm Zineb.



ST

$\frac{2.02}{20 \mu\text{m}} = 0.05 \mu\text{m}$

$20 \mu\text{m} \times \frac{1}{2} \times \frac{5 \mu\text{ml}}{5 \mu\text{ml}} = 10 \text{ mg injected.}$

$\frac{81}{105} \times 0.5 \text{ mg} = 0.385 \text{ mg}$

$\frac{0.385 \text{ mg}}{1 \text{ mg}} = 0.0385 \text{ ppm } \approx 77\%$

BHC

HP RUN # 49
AREA %

RT	AREA	AREA %
0.05	3320	0.019
0.52	10650000	59.422
0.89	626200	3.494
1.34	235300	1.313
2.03	238300	1.330
2.44	388600	2.168
4.35	284000	1.585
5.78	5497000	30.671

DIL FACTOR: 1.0000 E+ 0

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2cd. 5/1/86

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460
Analytical Chemistry Section
Building 402, ARC-East
Beltsville, Maryland 20705

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

April 24, 1986

MEMORANDUM:

SUBJECT: Registration Standard for Trifluralin. Method Trial

FROM: King Zee, Chemist *King Zee*
Analytical Chemistry Section

TO: Warren R. Bontoyan, Head *WRB*
Analytical Chemistry Section

A method trail on Trifluralin using PAM II Sec. 180207 procedure 5801210 and 5801110 is now completed. The requestor, Francis Griffith, Jr., RCB, HED, agreed via phone, 4/22/86, that single analysis of the fortified crops using procedure 5801210 is sufficient. Procedure 5801110 which has a TLC clean-up step was validated in duplicate samples.