Attachment 3517

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

Analytical Chemistry Section
Building 306, BARC-East
Beltsville, Maryland 20705

12-21-92 41823903

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

DEC 21 1992

MEMORANDUM

SUBJECT: PP#0F3918. SAN-582H In/On Field Corn Petition Method Validation Request

FROM: Douglas M. Swineford, Chemist DMS
Elmer Hayes, Chemist EH
Analytical Chemistry Section

THRU: Harvey K. Hundley, Head HKH
Analytical Chemistry Section

THRU: Donald A. Marlow, Chief DAM
Analytical Chemistry Branch

TO: Debra F. Edwards, Ph.D., Acting Chief
Chemistry Branch I - Tolerance Support
Health Effects Division

INTRODUCTION

The Analytical Chemistry Section was requested to run a method validation for the analysis of the herbicide SAN-582H (2-chloro-N-[(1-methyl-2-methoxy)ethyl]-N-(2,4-dimethyl-thien-3-yl)-acetamide in/on corn grain, corn fodder and corn forage at 0.01 ppm and 0.05 ppm with controls using the method "A Method for the Determination of Residues of SAN-582H in Corn and Soil Samples", T.R. Bade; Project No: 414108, Sandoz Crop Protection Corporation.

METHOD SUMMARY

SAN-582H is extracted with two 250ml portions of methanol:water (95:5). The combined organic extracts are cleaned up by solid phase extraction on a pre-packed reversed phase C-18 column. Further clean up is achieved by partition between water and toluene using an Extralute® column followed by chromatography on a silica gel column using increasing volumes of ethylacetate:cyclohexane (2:8) for pre-wash and elution. The eluate is concentrated and dissolved in toluene. Separation and quantification is performed by capillary column gas chromatography using an NP detector.

COMMENTS

1. Recovery data for corn grain samples were inconsistent. Three separate sets of analyses were required to achieve satisfactory results. We did not attempt to determine the reason for the inconsistency. Because of the possible variability of different batches of silica gel due to moisture content, etc., it is recommended that each batch of silica gel be calibrated with SAN-582H to determine that SAN 582H is quantitatively retrieved and a spiked reagent blank (no matrix) run with each set of samples to determine performance. However, the pesticide guidelines do not allow that this performance be utilized to compensate for method recovery.

2. An HP 5890 Series II G.C. equipped with a 30 M DB-17 Mega-bore (0.53 mm I.D.) capillary column, auto sampler and NP detector was used for quantitation.

3. A set of six samples can be extracted, cleaned-up by two chemists in 8 hours. GLC analysis will require approximately 30 minutes per injection using an autosampler.

4. The limit of detection from visual inspection of the chromatograms is estimated to be 0.001 ppm.

5. No special safety hazards were noticed. Normal laboratory safety procedures were followed.

6. Potassium permaganate is part of the list of reagents on page 33 of method. Potassium permaganate is not used and should be deleted from the list of reagents.

7. The methanol:water ratio is stated as 2:1 in section 4.2 of method; it should be 1:2.

8. The third sentence in section 4.4 - Prewash Procedure should read "ethyl acetate/cyclohexane" instead of "acetate/cyclohexane."

9. The formula for calculating the residues on page 40 uses a recovery factor. This is not allowed for a tolerance enforcement method per EPA's pesticide assessment guidelines and needs to be changed.

10. Section 4.2.2 of method needs to define how to evaporate the combined filtrates to ca. 300 ml.

11. If the above comments are taken into consideration and incorporated, the method would meet 40 CFR 158 and EPA's requirements as published in the Pesticide Assessment Guidelines, Subdivision "O" for Residue Chemistry, Part 171-4(b) as an enforcement method.

Commodity	Chemical Added	PPM Added	PPM Found	% Recovery
Corn Grain	Control	0	N.D.	
	Control	0	N.D.	
	SAN-582H	0.01	N.D.	
	SAN-582H	0.01	N.D.	
	SAN-582H	0.05	N.D.	
	SAN-582H	0.05	N.D.	
Corn Grain (2nd Analysis)	Control	0	N.D.	
	Control	0	N.D.	
	SAN-582H	0.01	0.0087	86.6
	SAN-582H	0.01	0.0098	98.4
	SAN-582H	0.05	0.0142	28.4
	SAN-582H	0.05	0.0086	17.3
Corn Grain (Analysis of 0.05ppm Extracts from 2nd Analysis)	SAN-582H	0.05	0.0157	31.5
	SAN-582H	0.05	0.0111	22.3
Corn Grain (3rd Analysis)	SAN-582H	0.05	0.0450	89.9
	SAN-582H	0.05	0.0501	100.
Corn Fodder	Control	0	N.D.	
	Control	0	N.D.	
	SAN-582H	0.01	0.0098	97.5
	SAN-582H	0.01	0.0072	72.0
	SAN-582H	0.05	0.0342	68.5
	SAN-582H	0.05	0.0284	56.9

Corn Fodder	SAN-582H	0.05	0.0410	82.1
(2nd Analysis)	SAN-582H	0.05	0.0459	91.9
Corn Forage	Control	0	N.D.	
	Control	0	N.D.	
	SAN-582H	0.01	0.0103	103.
	SAN-582H	0.01	0.0106	106.
	SAN-582H	0.05	0.0444	88.8
	SAN-582H	0.05	0.0470	94.0

Control = Commodity Only (No Spike)
N.D. = <0.001 ppm

Modifications Made to Method:

None

Special Precautions to be Taken:

None

Source of Analytical Reference Standards:

Standards were obtained from the petitioner

If derivatized standards used, give source:

None

Instrument for Quantitation:

HP 5890 Series II, equipped with NP detector

Instrument for Confirmation:

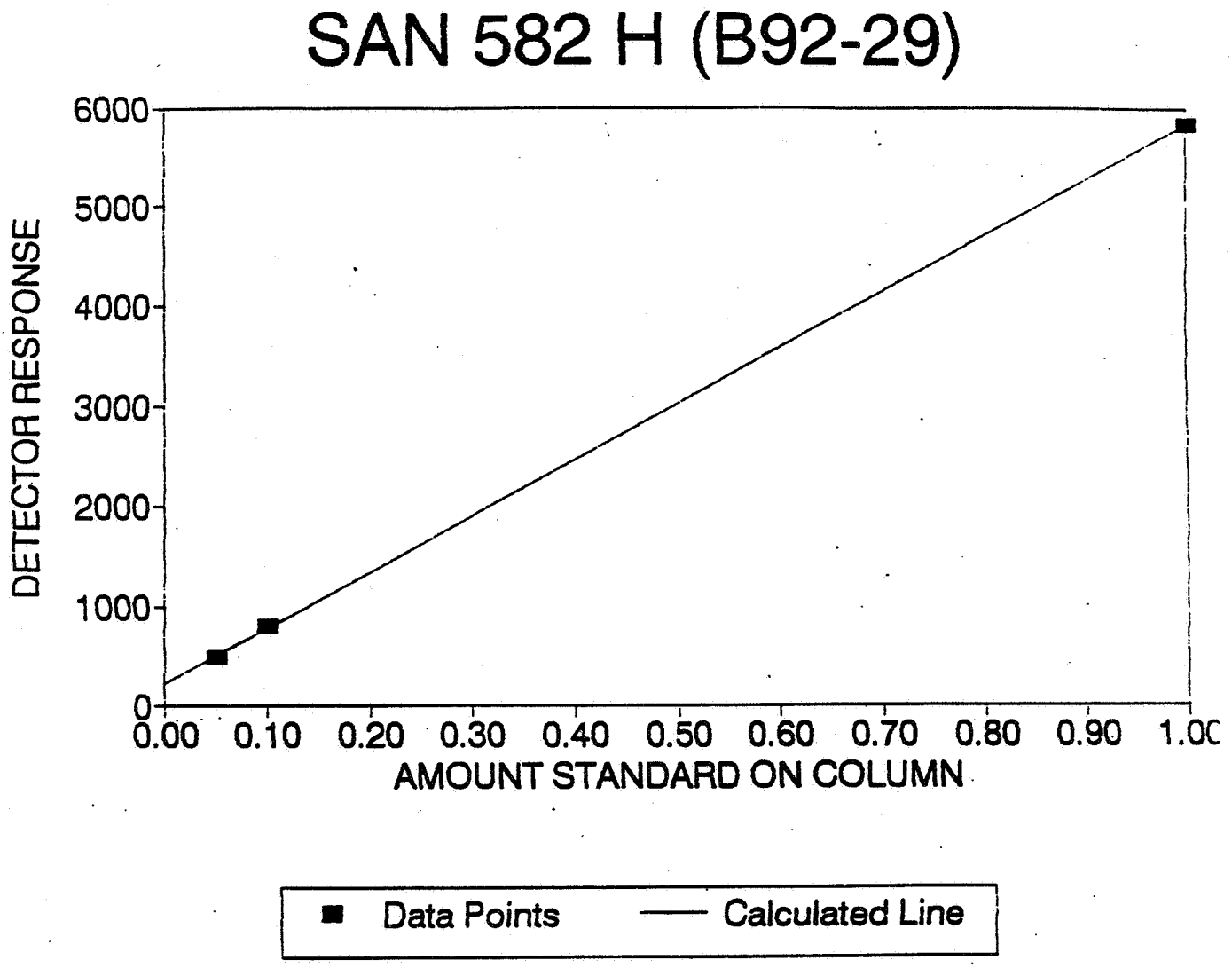
None

If instrument parameters differ from those in Method, list parameters actually used:

No deviations

Commercial source for any special chemicals or apparatus:

No special chemicals or apparatus involved.


SAN 582 H (B92-29)
DETECTOR RESPONSE
6000
5000
4000
3000
2000
1000
0
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
AMOUNT STANDARD ON COLUMN
Data Points
Calculated Line

** LINEAR REGRESSION **

Project #: B92-29
Compound: SAN 582 H
Date: 11/10/92
Analyst: DMS
Instrument: GC
Detector: NPD
Inj Volume: 3
Misc. Info:

	UG/ML Std on Col	PK/HT 1	PK/HT 2	Area 3	Area Average	Area /Amount
STD 1	0.0500	446	518		482	9640
STD 2	0.1000	863	747		805	8050
STD 3	1.0000	5865	5797		5831	5831

Regression Output:

			CALC.
Constant	222.17784	X Values	Y Values
Std Err of Y Est	30.08598	=====	======
R Squared	0.9999497	0.050	503
No. of Observations	3	0.100	783
Degrees of Freedom	1	1.000	5832
		0	222.17784
X Coefficient(s)	5609.9708		
Std Err of Coef.	39.791721		

1st RUN of CORN GRAIN (1)

TRACE @ 0.05

B92-29 SAN-582H

Corn Grain 25g Sample aliquot

Final Vol. all Samples 2 ml

3 ul inj - all.

```
FRONT INJECTOR
 INJ BOTTLE                    1
 FIRST BOTTLE                  1
 LAST BOTTLE                  10
 # OF SAMPLE WASHES            3
 # OF PUMPS                    3
 VISCOSITY                     0
 VOLUME                        3
 # OF SOLVENT A WASHES         3
 # OF SOLVENT B WASHES         3
 PRIORITY SAMPLE  1= ES        0
 CHAILLEX ON-COLUMN            0

*  SEQ  STRT

 Waiting for System Readiness
RUN #  150      NOV 17, 1992  11:53:44
STRPT
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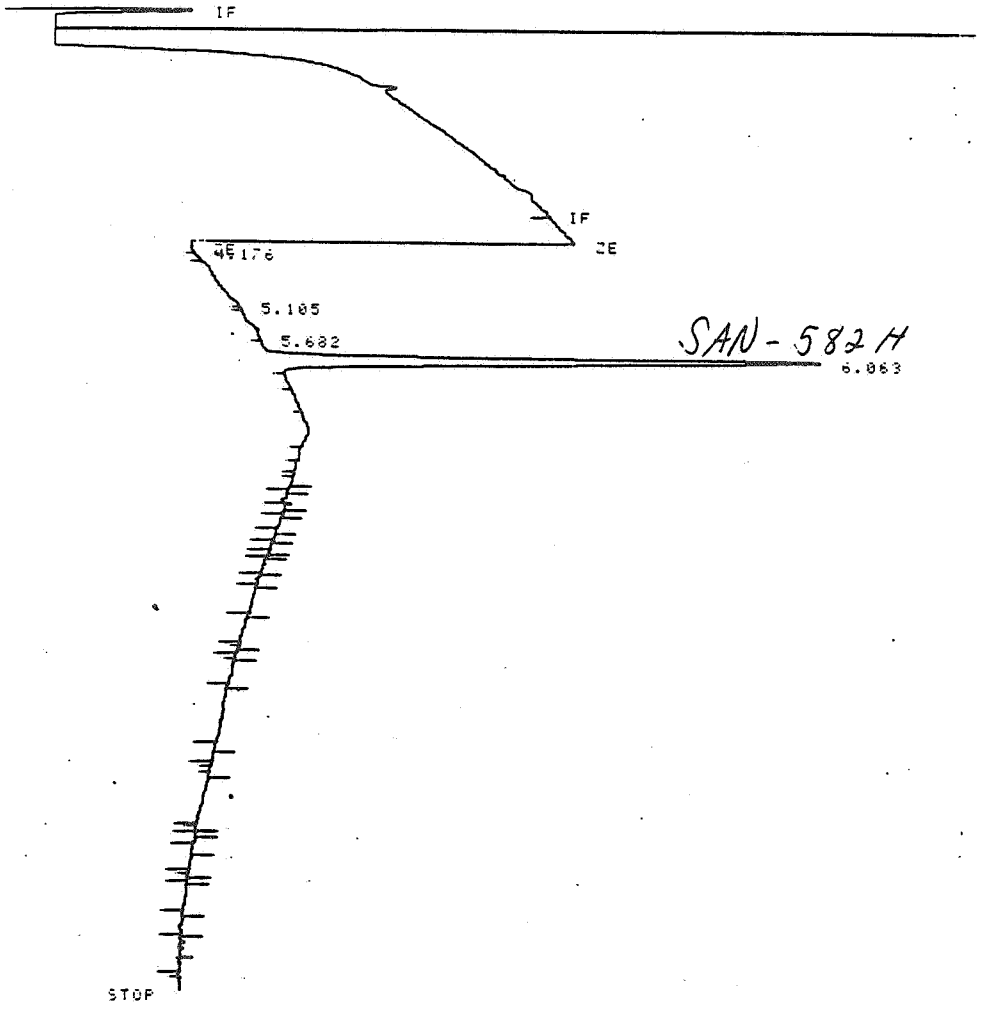


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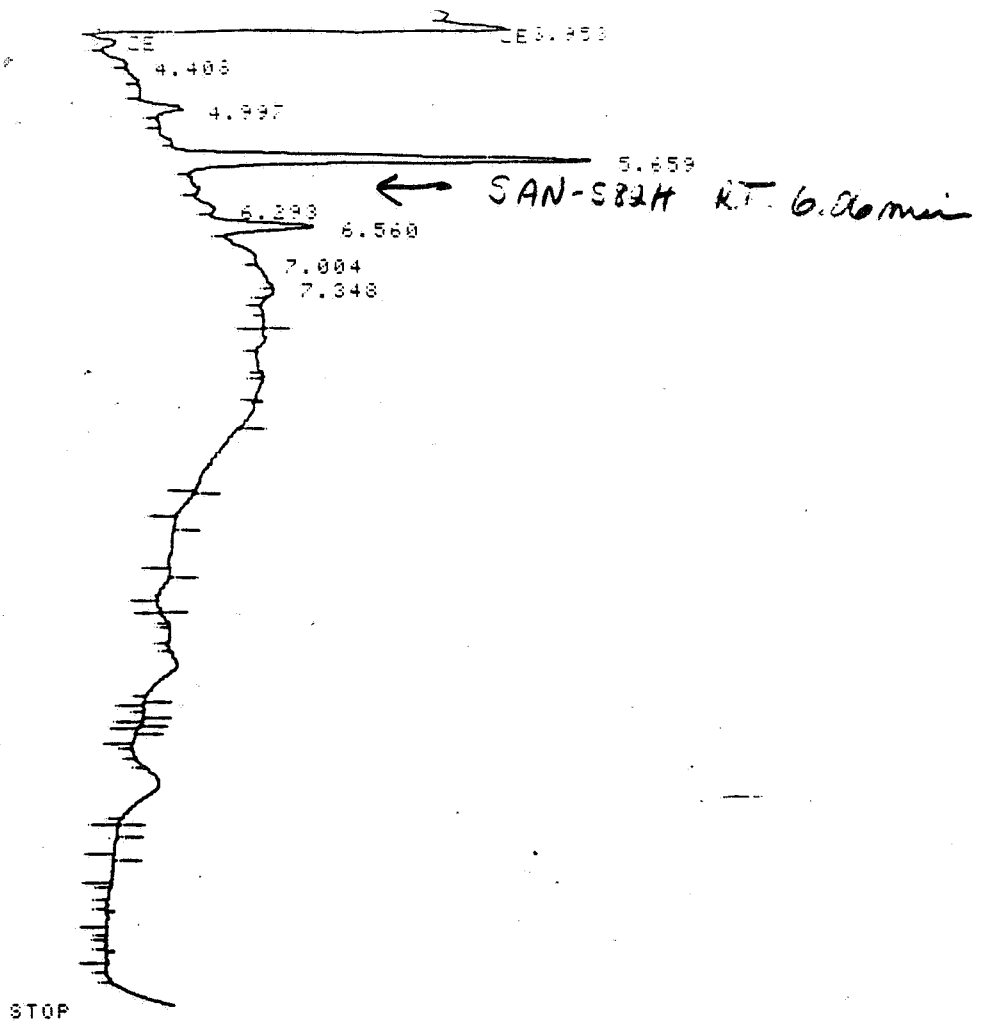


losing signal file A:Q5835B16.BNC

JN# 153 NOV 17, 1992 12:56:53

AMPLE NAME: B92-29 SAMPLE# 2
ORN GRAIN CONTROL(25G ALIQUOT) 3UL INJ

IGNAL FILE: A:Q5835B16.BNC

92-29: SAN 582H: DB-17 MEGABORE COL

STD-AREA

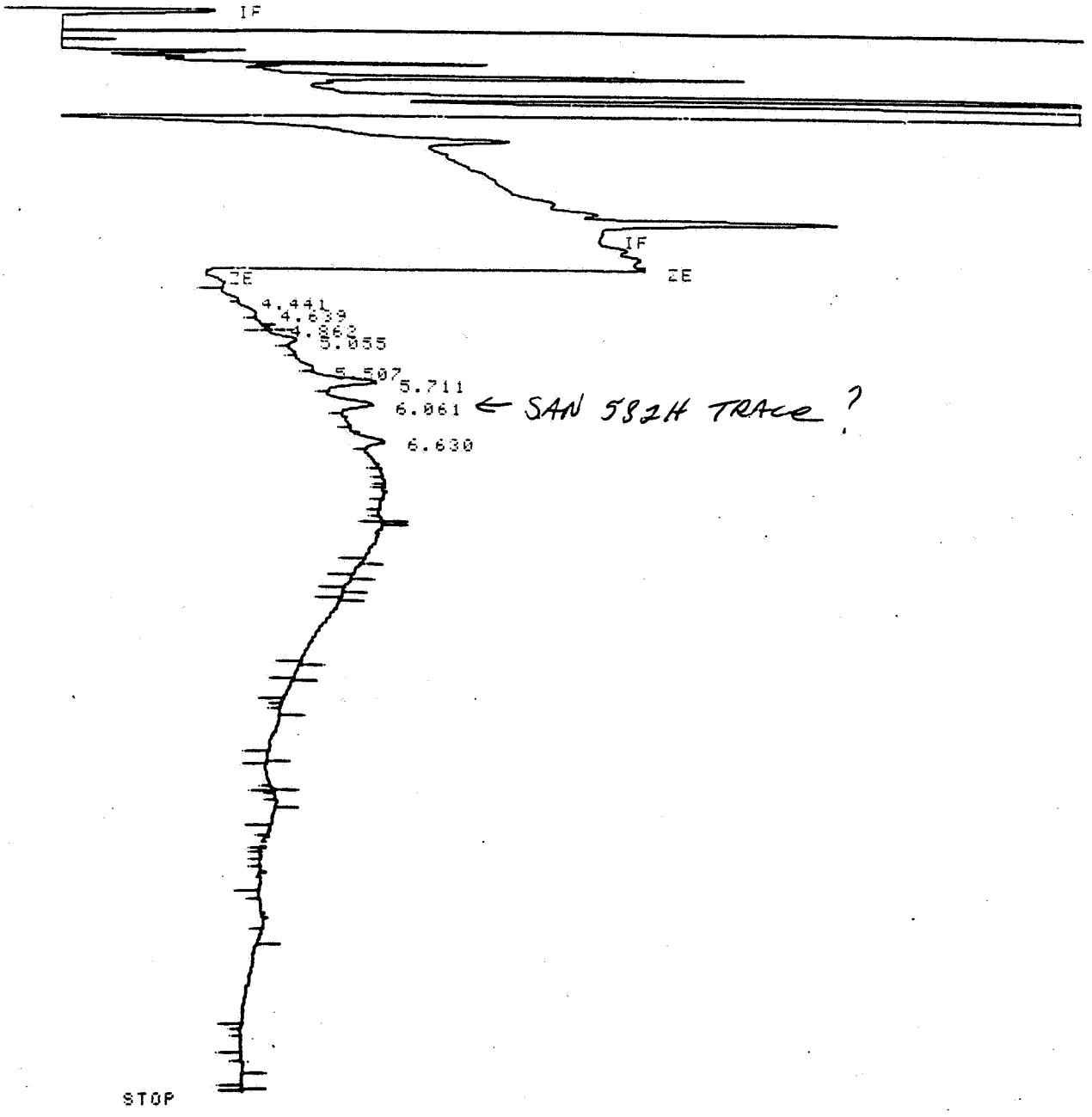
RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	AMOUNT	NAME
6.293	VV	1893	.192	164	1R	.004	SAN 582H

OTAL AREA= 45954
/L FACTOR=1.0000E+00

IN # 154 NOV 17, 1992 13:18:14
ART

IF

RUN # 165 NOV 1 1992 17:13:29
START



← SAN 582H TRACE ?

Closing signal file A:Q583973A.BNC

RUN# 165 NOV 17, 1992 17:13:29

SAMPLE NAME: B92-29 SAMPLE# 8
CORN GRAIN SPK 0.05 PPM #1 (25G ALIQUOT) 3UL INJ

SIGNAL FILE: A:Q583973A.BNC

B92-29: SAN 582H; DB-17 MEGABORE COL

ESTD-AREA

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	AMOUNT	NAME
6.061	VV	5938	.200	495	1R	.014	SAN 582H

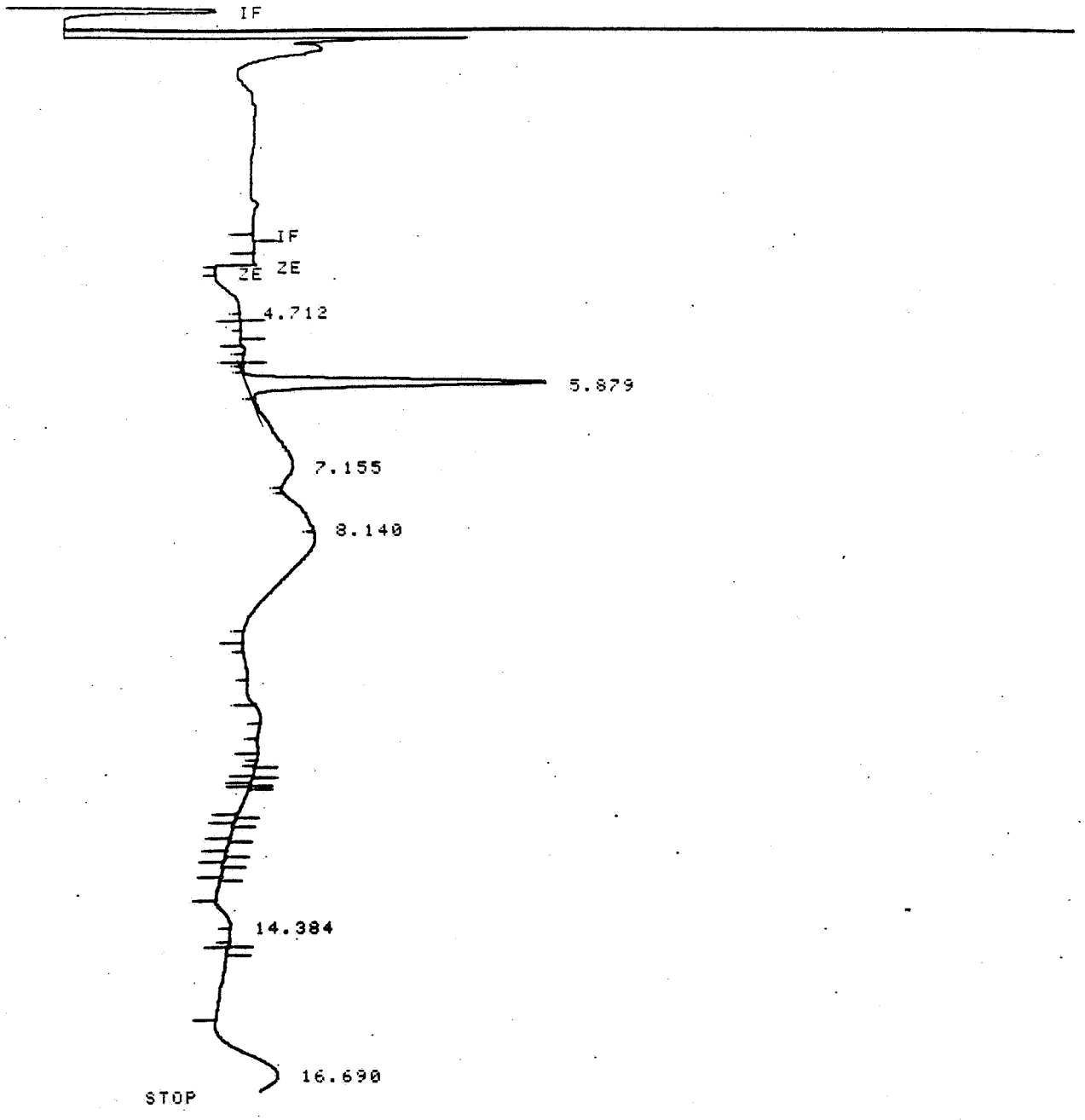
TOTAL AREA= 22682
MUL FACTOR=1.0000E+00

9.171	698	VV	1.163	9.78002	
12.030	400	PW	.552	5.60460	
13.581	264	VP	15	3.69903	
16.730	3781	I BM	.561	38.96595	

TOTAL HEIGHT= 7137
MUL FACTOR=1.0000E+00

CORN GRAIN (2)

RUN # 244 NOV 23, 1992 23:02:51
START



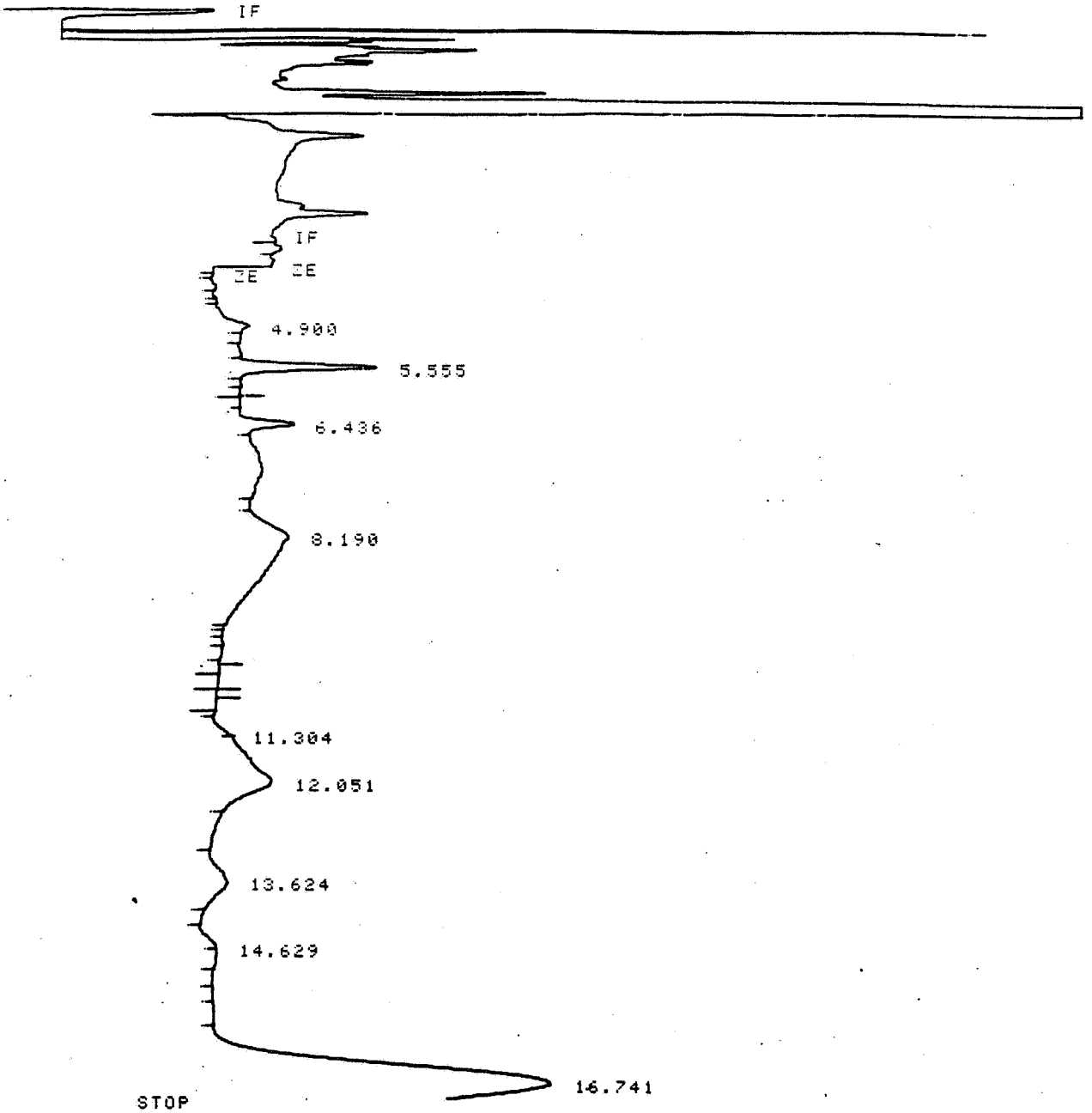
RUN# 244 NOV 23, 1992 23:02:51

SAMPLE NAME: 892-29 SAMPLE# 10
0.5UG/ML STD / 3UL INJ (SAN 582H)

892-29: SAN 582H: DB-17 MEGABORE COL

CON GRAIN B

RUN #. 242 NOV 23, 1992 22:20:04
START



RUN# 242 NOV 23, 1992 22:20:04

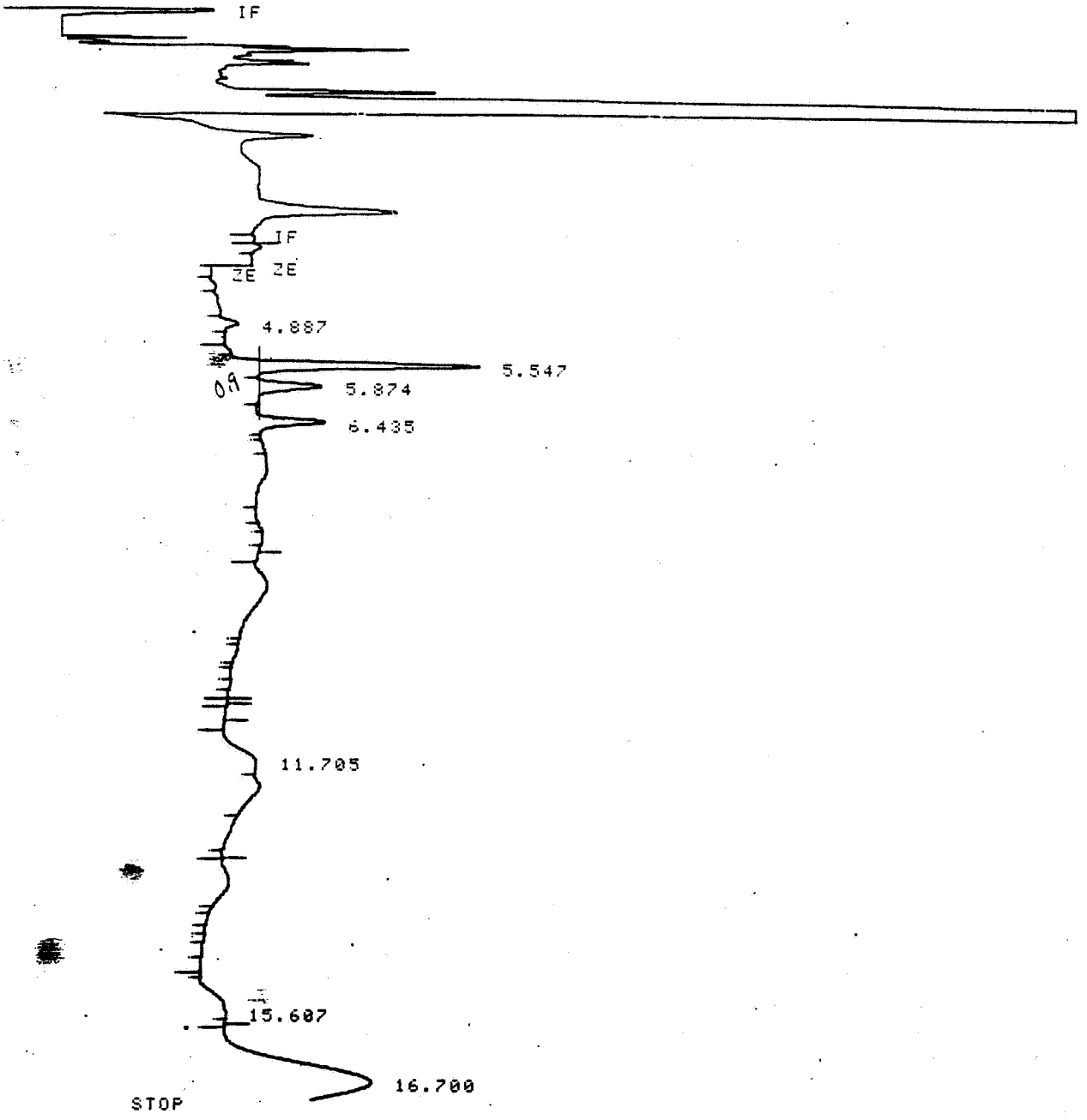
SAMPLE NAME: B92-29 SAMPLE# 9
~~CORN GRAIN STALK 0.05PPM~~ 100G/2ML(B)
CONTROL CORN GRAIN (A)

B92-29: SAN 582H: DB-17 MEGABORE COL

NO CALIB PEAKS FOUND
HEIGHT%

RT	HEIGHT	TYPE	WIDTH	HEIGHT%
4.900	229	PV	.180	3.64998
5.555	1195	VV	.122	19.04686
6.436	482	PV	.144	7.68250
8.190	502	VV	.983	8.00127
11.304	162	PV	.139	2.58208

RUN # 236 NOV 23, 1992 20:11:45
START



RUN# 236 NOV 23, 1992 20:11:45

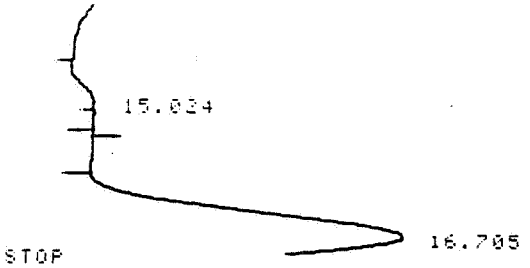
SAMPLE NAME: B92-29 SAMPLE# 6
CORN GRAIN SPIKE, 0.01PPM-100G/2ML(B)

B92-29; SAN 582H; DB-17 MEGABORE COL

ESTD-AREA

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	AMOUNT	NAME
5.874	VV	8865	.195	757	1	.021	SAN 582H

TOTAL AREA= 82498
MUL FACTOR=1.0000E+00



RUN# 240 NOV 23, 1992 21:37:19

SAMPLE NAME: B92-29 SAMPLE# 8
CORN GRAIN SPIKE, 0.05PPM-100G/2ML(A)

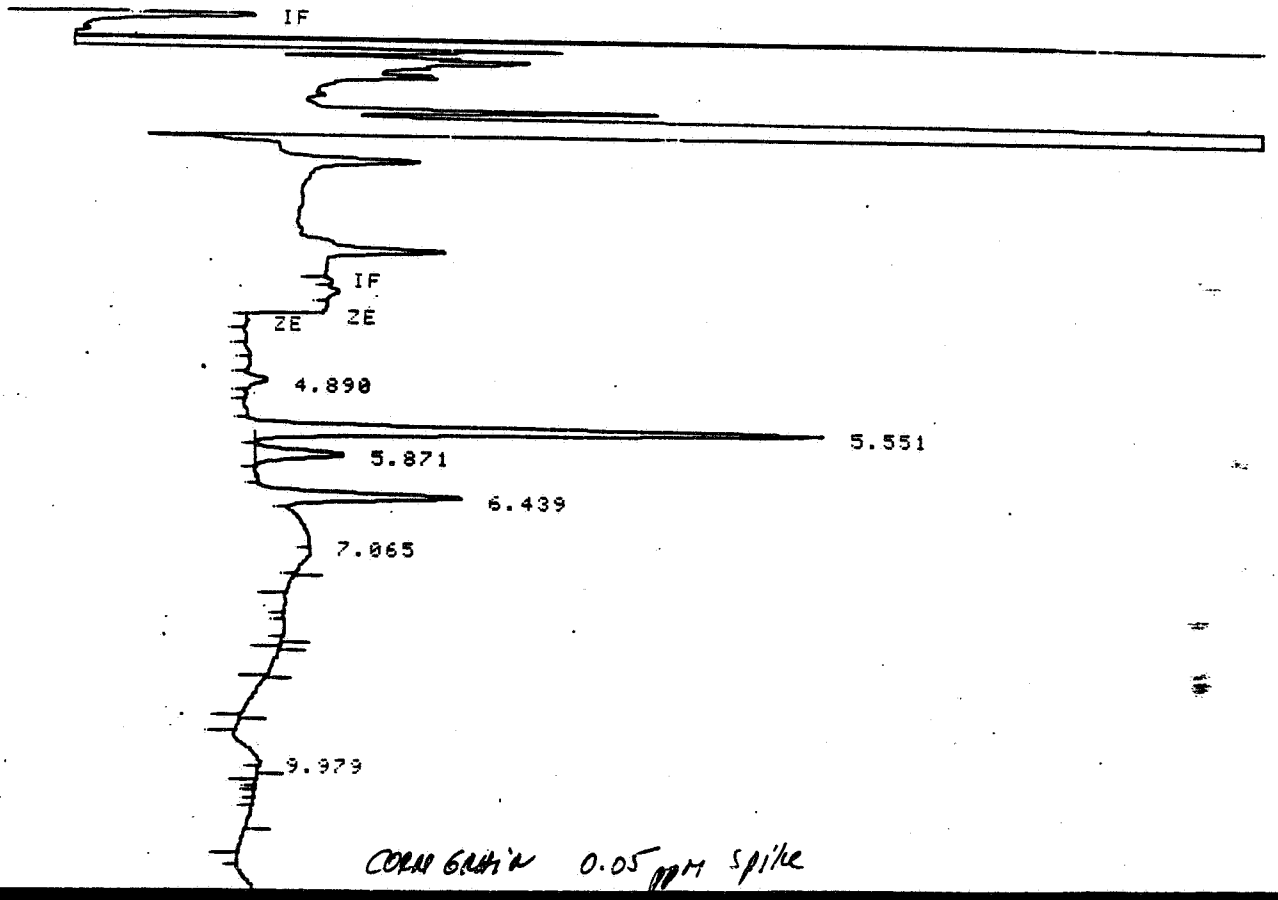
B92-29; SAN 582H; DB-17 MEGABORE COL

ESTD-AREA

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	AMOUNT	NAME
5.877	VV	7452	.164	759	1	.017	SAN 582H

TOTAL AREA= 145442
MUL FACTOR=1.0000E+00

RUN # 241 NOV 23, 1992 21:58:43
START

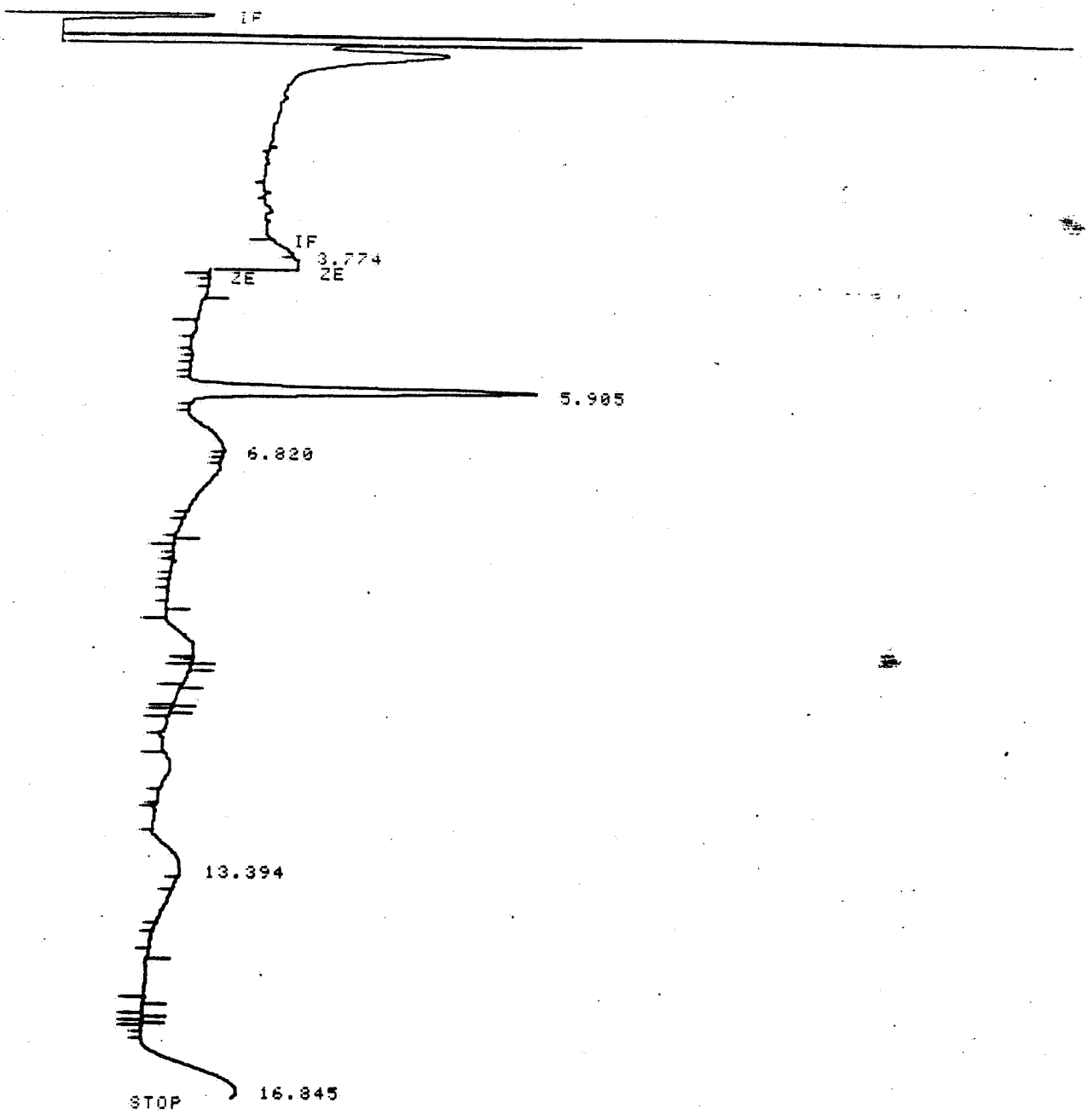


CORN GRAIN 0.05 ppm spike

TOTAL AREA= 13[illegible]81
MUL FACTOR=1.0000E+00

Solution 3.05 (4)
Repeat

RUN # 272 DEC 7, 1992 11:53:22
START



RUN# 272 DEC 7, 1992 11:53:22

SAMPLE NAME: B92-29 SAMPLE# 1
STD. 582H, 0.5UG/ML, 3UL INJ.

B92-29: SAN 582H: DB-17 MEGABORE COL

ESTD-AREA

RT TYPE AREA WIDTH OUTPUT AMOUNT

15

SAMPLE NAME: B92-29
STD. 582H, 0.5UG/ML 3UL INJ.

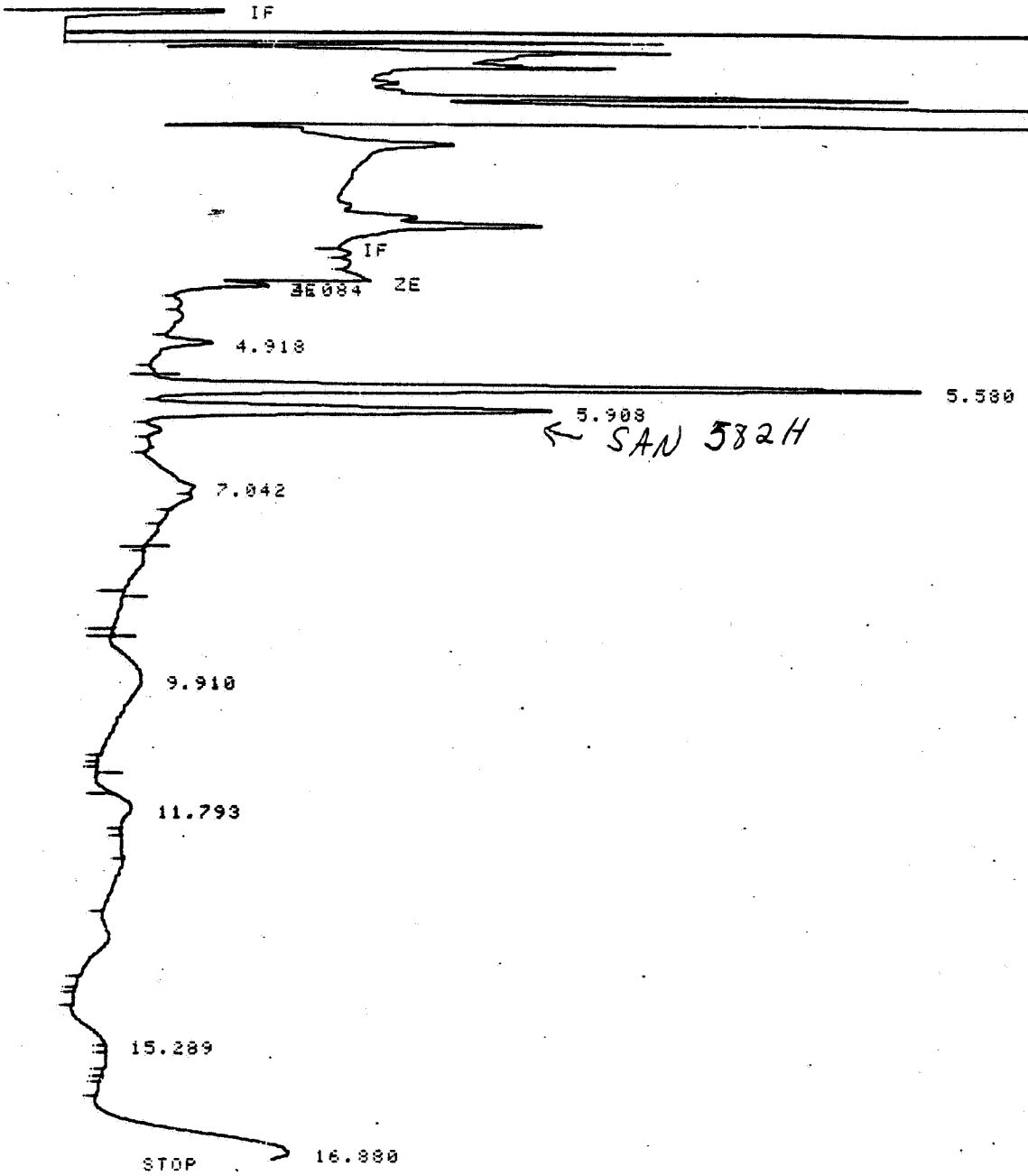
B92-29: SAN 582H: DB-17 MEGABOPE COL

ESTD-AREA

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	AMOUNT	NAME
5.905	VV	22106	.126	2914	1	.051	SAN 582H

TOTAL AREA= 62821
MUL FACTOR=1.0000E+00

RUN # 273 DEC 7, 1992 12:14:47
START



16

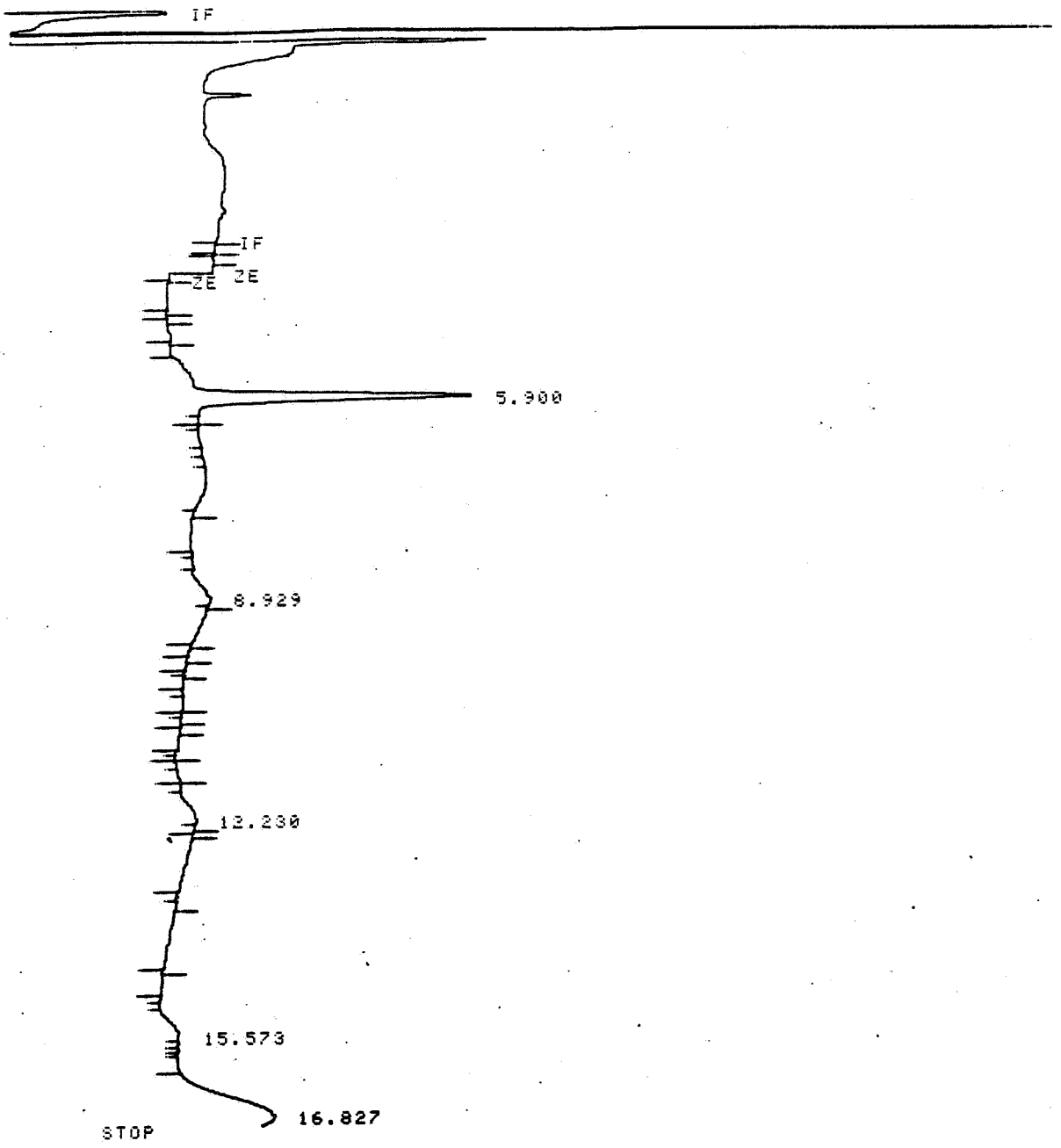
FACTOR=1.0000E+00

Corn Thaw 2.25 3

Std

N # 267 NOV 27, 1992 13:11:52

HRT



UN# 267 NOV 27, 1992 13:11:52

AMPLE NAME: B92-29 SAMPLE# 4
TD. 582H, 0.5UG/ML, 3UL INJ.

92-29: SAN 582H: DB-17 MEGABORE COL

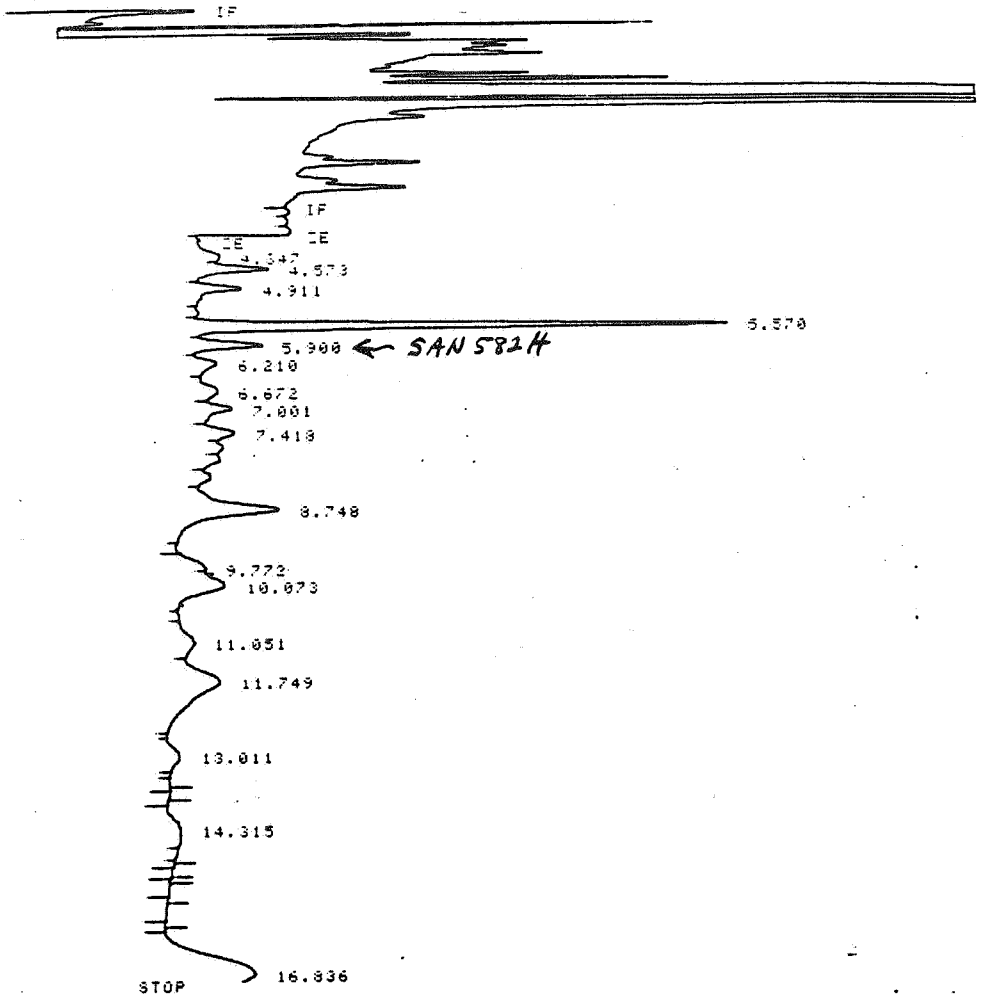
TD-AREA

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	AMOUNT	NAME
5.900	BV	20611	.150	2297	1	.048	SAN 582H

17

WKN 0kum 0.05 (5)

RUN # 263 NOV 27, 1992 11:46:26
STRPT



RUN# 263 NOV 27, 1992 11:46:26

SAMPLE NAME: B92-29 SAMPLE# 2
REPEAT CORN GRAIN, 0.05-1PPM, 2ML,25G SPL

B92-29; SAN 582H; 08-17 MEGABORE COL

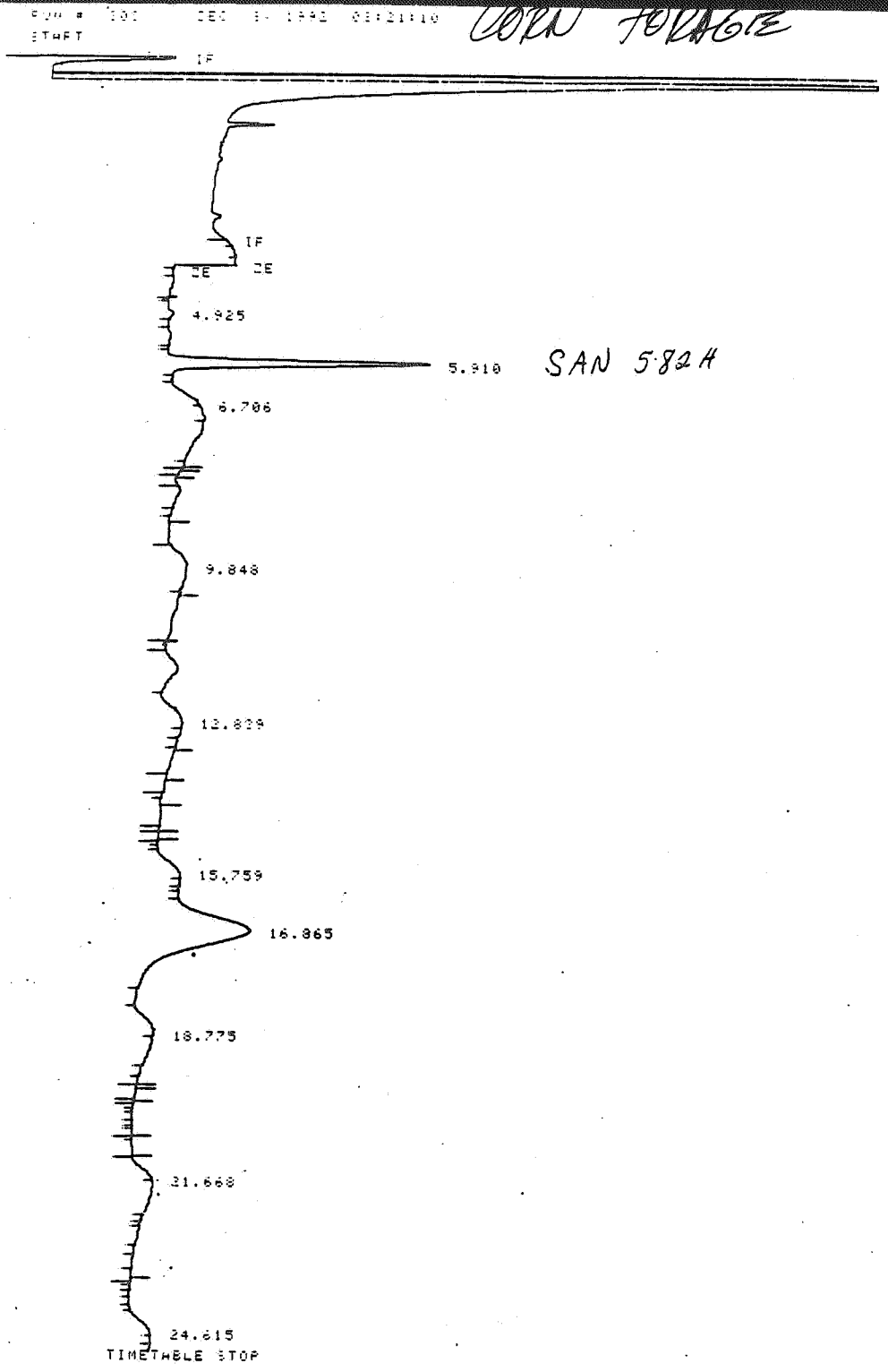
ESTD-AREA

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	AMOUNT	NAME
5.900	VV	6649	.154	721	1	.015	SAN 582H

TOTAL AREA= 162457
MUL FACTOR=1.0000E+00

RUN # 264 NOV 27, 1992 12:07:47
STRPT

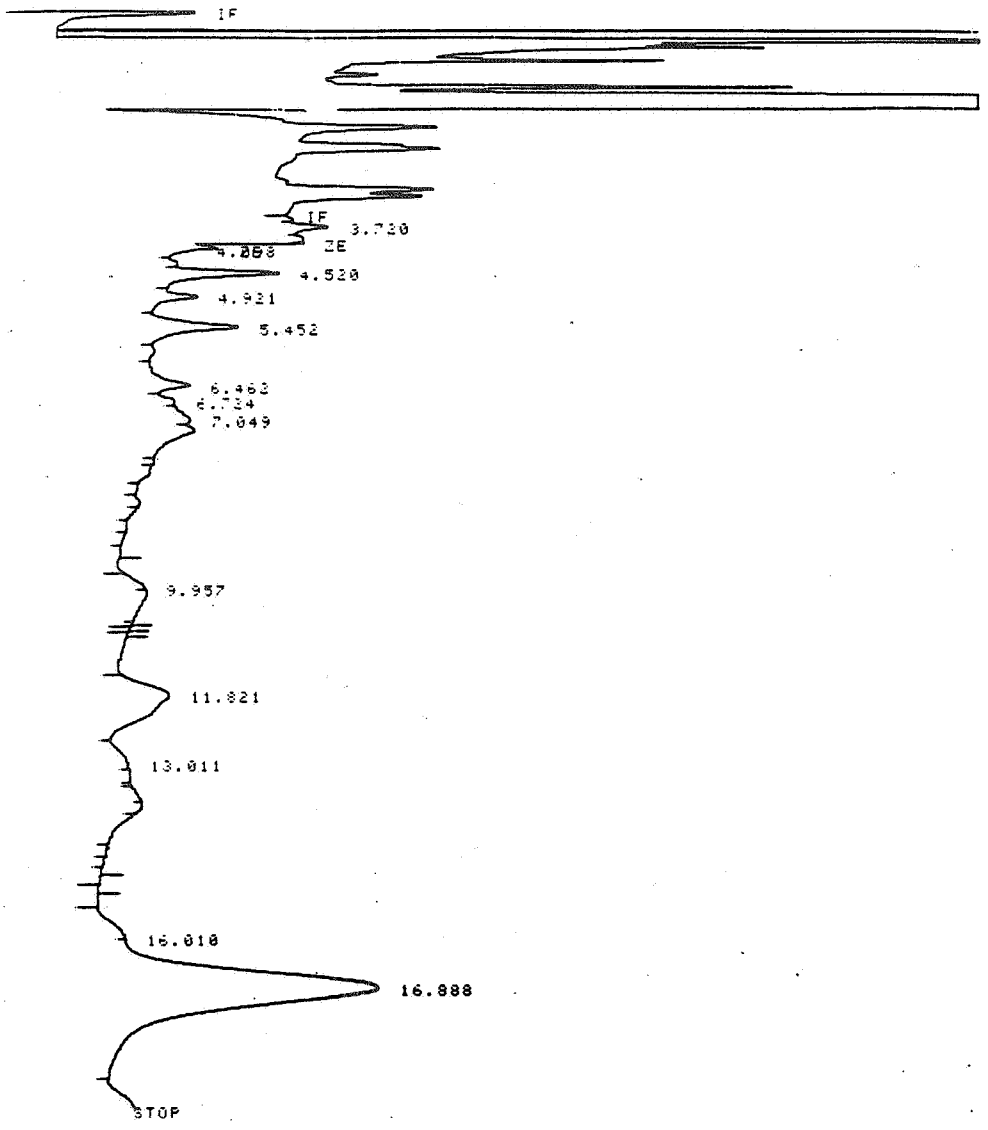
CORN FORAGE


RUN # 101 DEC 3- 1992 03:21:10
START
IF
IF
DE
DE
4.925
5.910
SAN 5824
6.706
9.848
13.839
15.759
16.865
18.775
21.668
24.615
TIMETABLE STOP

15.511	[illegible]	P	.441	[illegible]
16.393	3649	VP	.700	32.296899
16.464	107	P	.363	1.30456

TOTAL HEIGHT= 3203
NOL FACTOR=1.0000E+00

RUN # 306 DEC 8, 1992 09:37:17
START



RUN# 306 DEC 8, 1992 09:37:17

SAMPLE NAME: B92-29 SAMPLE# 2
CORN FORAGE-CONTROL #1(3UL INJ/2ML FINAL VOL/25G)

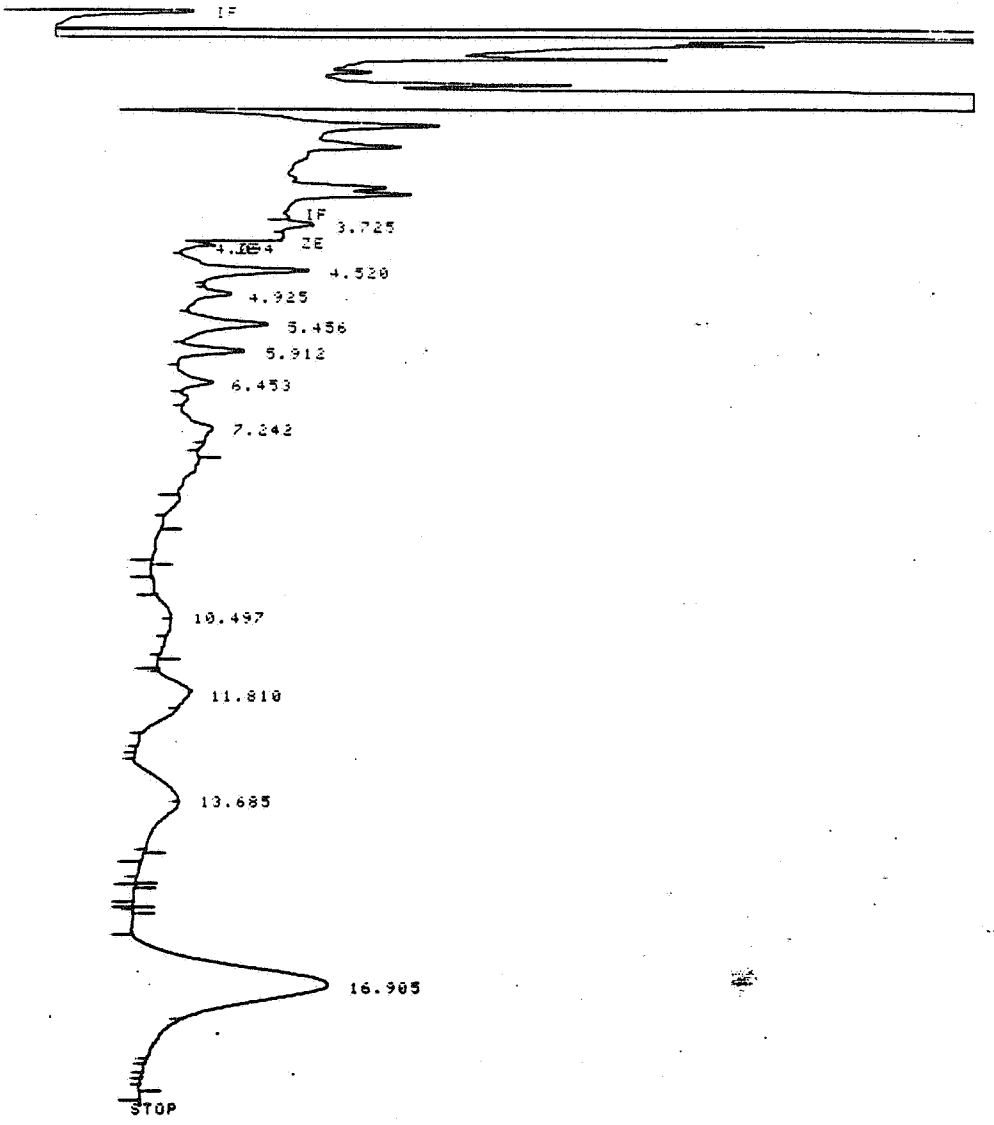
B92-29; SMN 582M; DB-17 MEGABORE COL

PEAKS FOUND

MIDTH HEIGHT

TOTAL AREA= 73114
MUL FACTOR=1.0000E+00

RUN # 311 DEC 8, 1992 11:34:05
STRT



RUN# 311 DEC 8, 1992 11:34:05

SAMPLE NAME: 892-29 SAMPLE# 5
CORN FORAGE-0.01PPM SPK #1(3UL INJ/2ML FINAL VOL/25G ALIQUOT)

892-29: SAN 582H: DB-17 MEGABORE COL

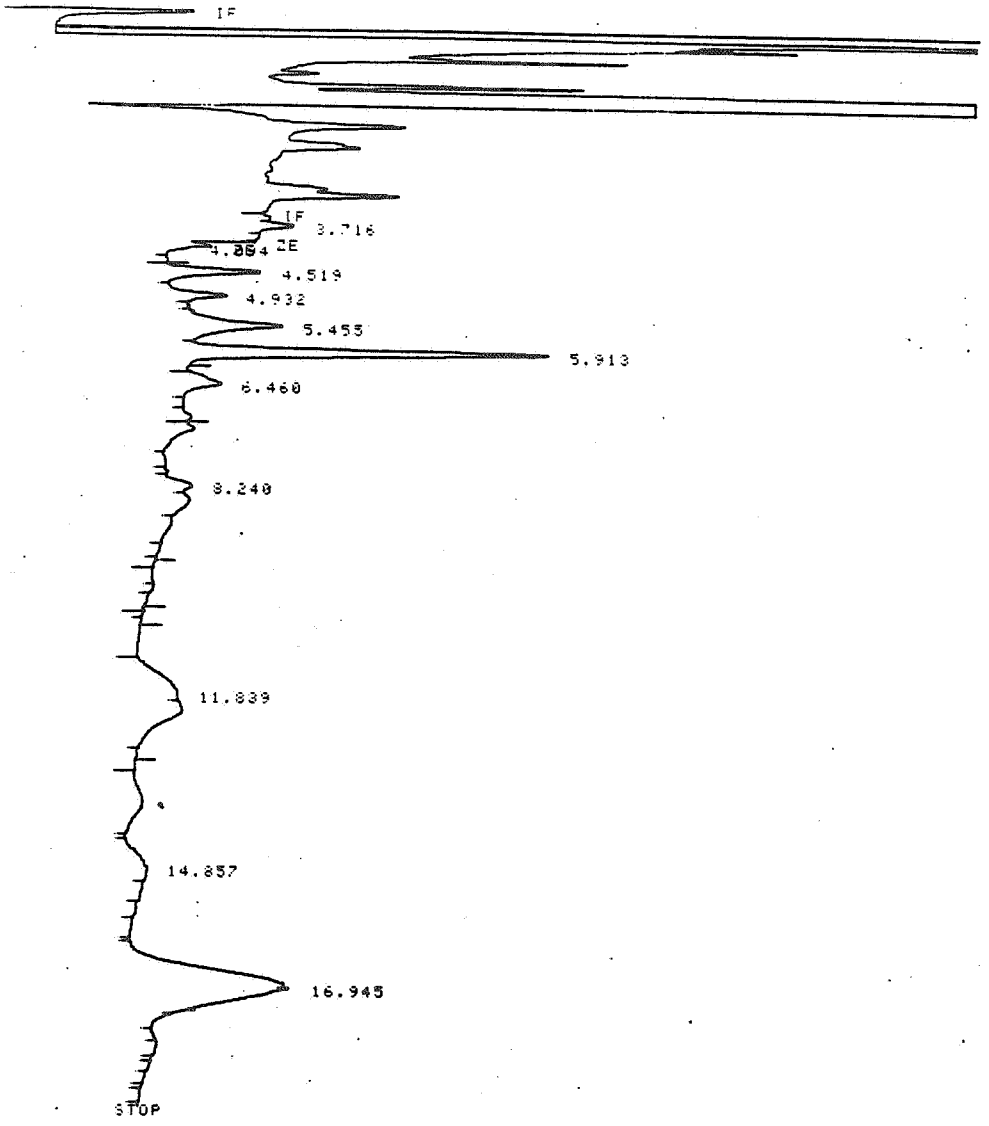
ESTD-AREA

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	AMOUNT	NAME
5.912	VP	5148	.135	636	1	.012	SAN 582H

TOTAL AREA= 146603
MUL FACTOR=1.0000E+00

TOTAL AREA= 174419
MUL FACTOR=1.0000E+00

RUN # 319 DEC 8, 1992 14:40:58
START



RUN# 319 DEC 8, 1992 14:40:58

SAMPLE NAME: B92-29 SAMPLE# 9
CORN FORAGE-0.05PPM SPK #2(30UL INJ/2ML FINAL VOL/25G ALIQUOT)

B92-29: SAN 582H: DB-17 MEGABORE COL

ESTD-AREA

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	AMOUNT	NAME
5.913	VB	26292	.131	3348	1	.061	SAN 582H

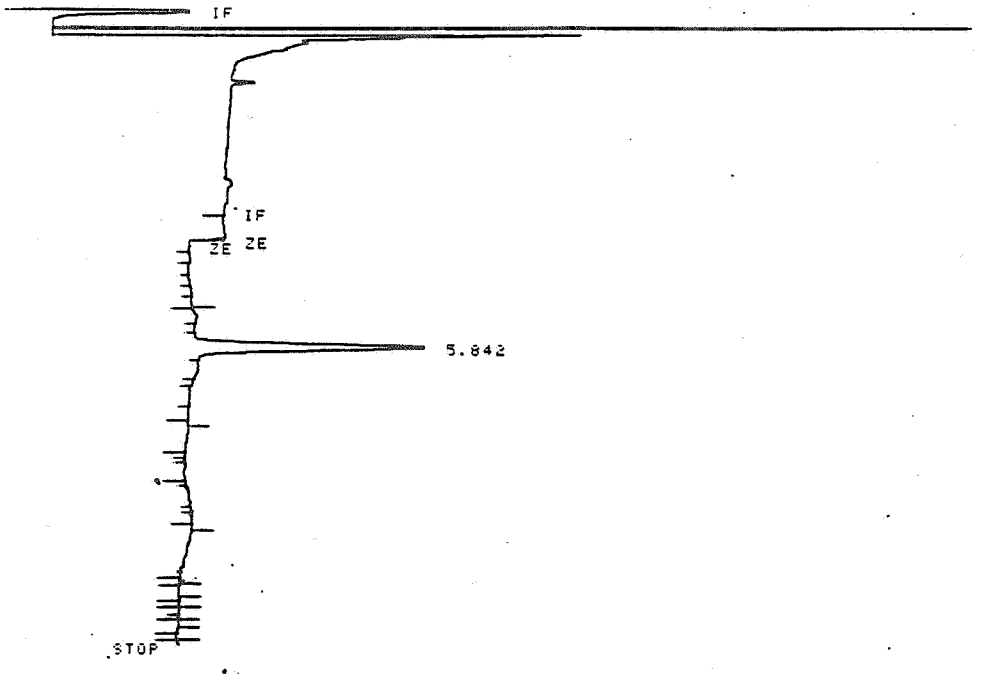
Corn Fodder B92 29

Corn Fodder

SAN-582H

* SEQ START

Waiting for System Readiness
RUN # 303 NOV 19, 1992 10:33:41
START



Closing signal file A:0585DC86.BNC

RUN# 303 NOV 19, 1992 10:33:41

SAMPLE NAME: B92-29 SAMPLE# 1
0.5UG/ML STD/3UL INJ(SAN 582H)

SIGNAL FILE: A:0585DC86.BNC

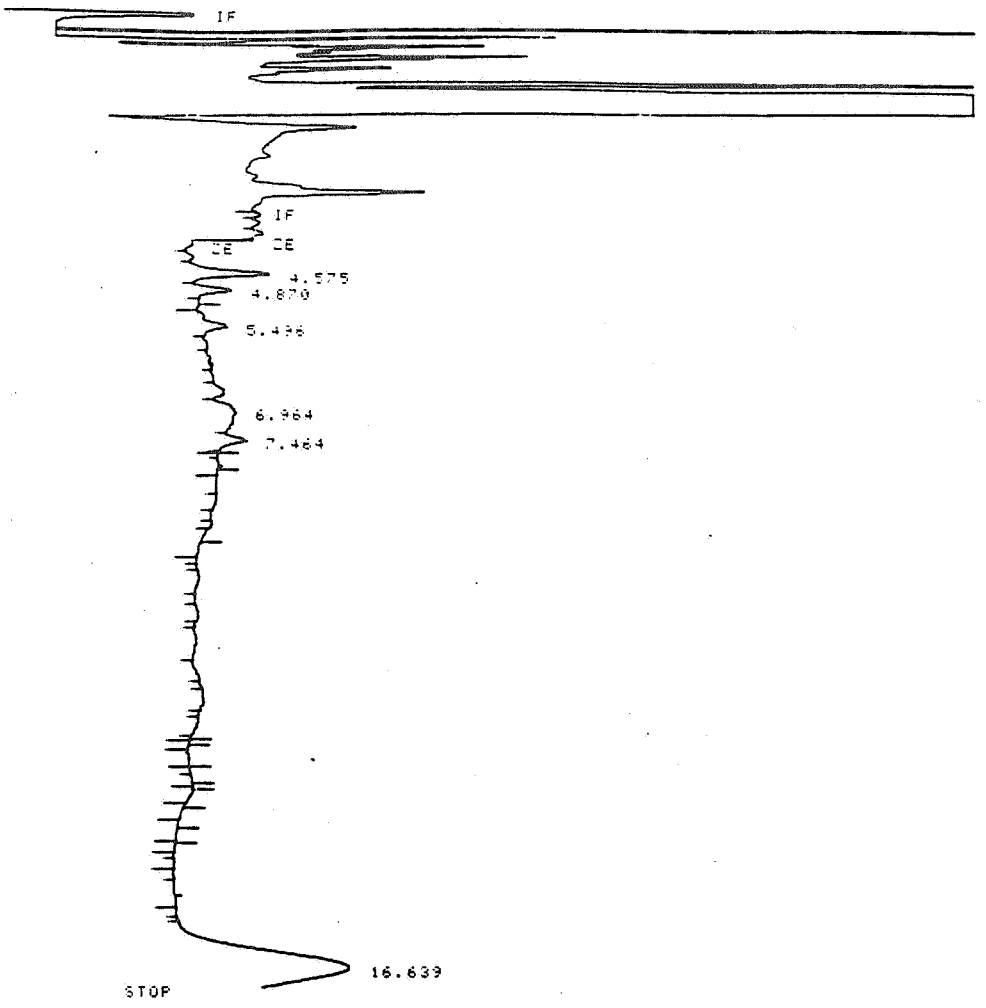
B92-29: SAN 582H: DB-17 MEGABORE COL

ESTD-AREA

PT	TYPE	AREA	WIDTH	HEIGHT	CAL#	AMOUNT	NAME
5.842	VV	17568	.137	2143	1	.041	SAN 582H

TOTAL AREA= 17568
MUL FACTOR=1.0000E+00

RUN # 209 NOV 19, 1992 12:08:41
STHRT



Closing signal file A:0585F2CA.BNC

RUN# 209 NOV 19, 1992 12:08:41

SAMPLE NAME: B92-29 SAMPLE# 3
CORN FODDER-CONTROL/12.5G ALIQUOT/FINAL VOL 1ML/3UL INJ

SIGNAL FILE: A:0585F2CA.BNC

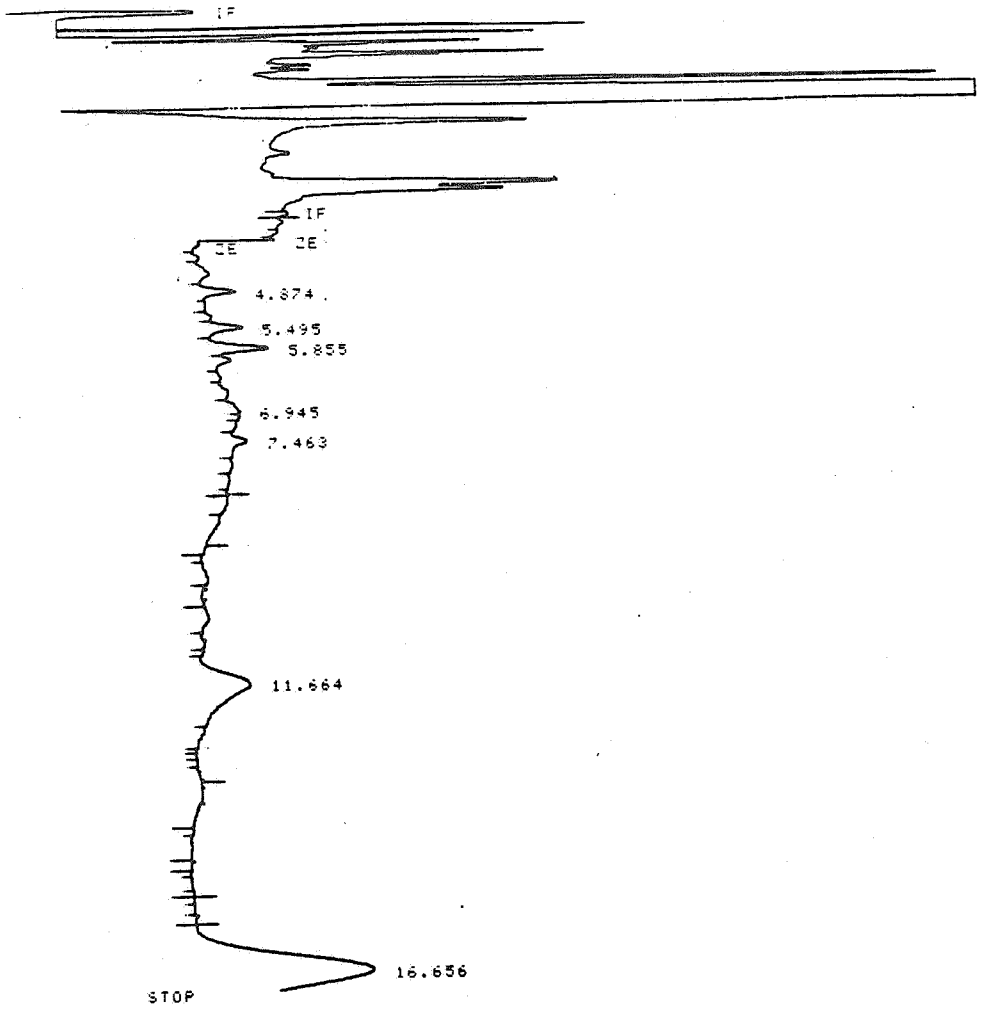
B92-29: SAN 582H: DB-17 MEGABORE COL

NO CALIB PEAKS FOUND
HEIGHT%

RT	HEIGHT	TYPE	WIDTH	HEIGHT%
4.575	724	PV	.131	21.30038
4.870	336	VV	.111	9.88526
5.496	261	BV	.162	7.67873
6.964	222	VV	.414	6.53133
7.464	279	VV	.166	8.20830
16.639	1577	I VH	.610	46.39600

TOTAL HEIGHT= 3399
MUL FACTOR=1.0000E+00

RUN # 213 NOV 19, 1992 13:34:01
START



Closing signal file A:Q58606C9.BNC

RUN# 213 NOV 19, 1992 13:34:01

SAMPLE NAME: B92-29 SAMPLE# 5
CORN FODDER-0.01 SPK/12.5G ALIQUOT/FINAL VOL 1ML/3UL INJ

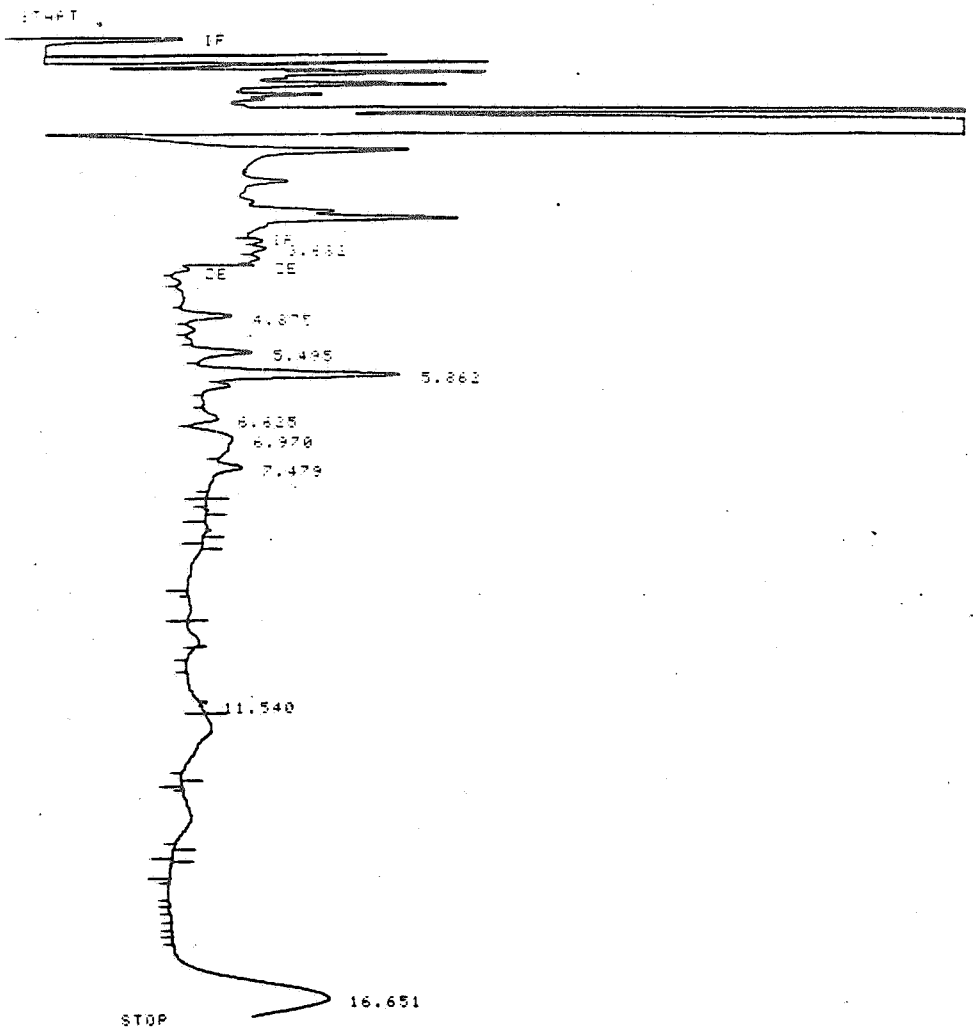
SIGNAL FILE: A:Q58606C9.BNC

B92-29: SAN 582H: DB-17 MEGABORE COL

ESTD-AREA

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	AMOUNT	NAME
5.855	VV	4664	.139	561	1	.011	SAN 582H

TOTAL AREA= 57445
MUL FACTOR=1.0000E+00



Closing signal file A:Q58624C6.BNC

RUN# 219 NOV 19, 1992 15:41:57

SAMPLE NAME: B92-29 SAMPLE# 8
CORN FODDER-0.05PPM SPK/12.5G ALIQOT/FINAL VOL 1ML/3UL INJ

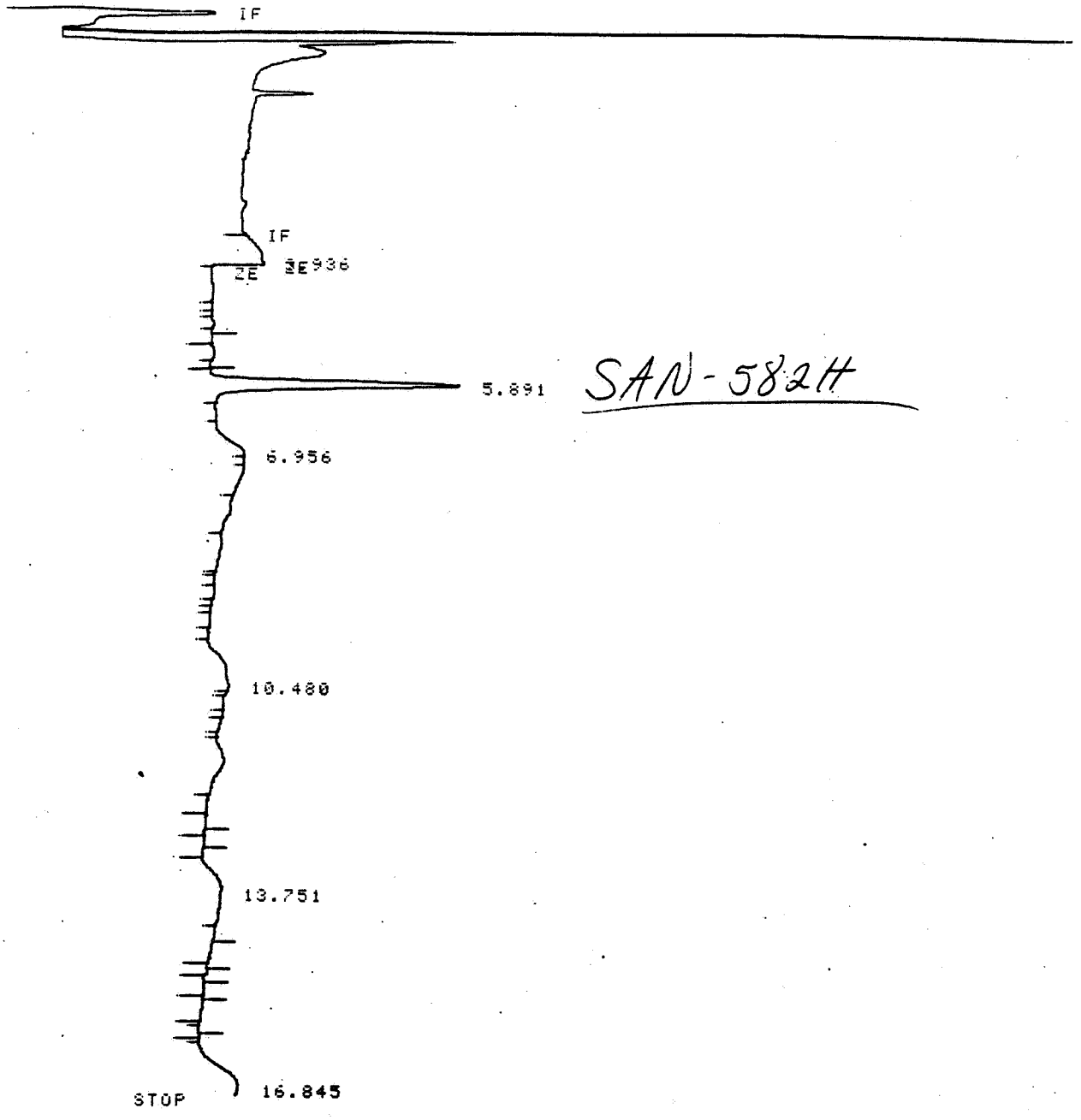
SIGNAL FILE: A:Q58624C6.BNC

B92-29: SAN 582H: DB-17 MEGABORE COL

RECALIBRATION [Y/N*]:
NAME: B92-29
REPORT MEMO: STD. 582H, 0.5UG/ML, 3UL INJ.

BOTTLE # : BREAK

* SEQ START
RUN # 253 NOV 25, 1992 13:35:36
START



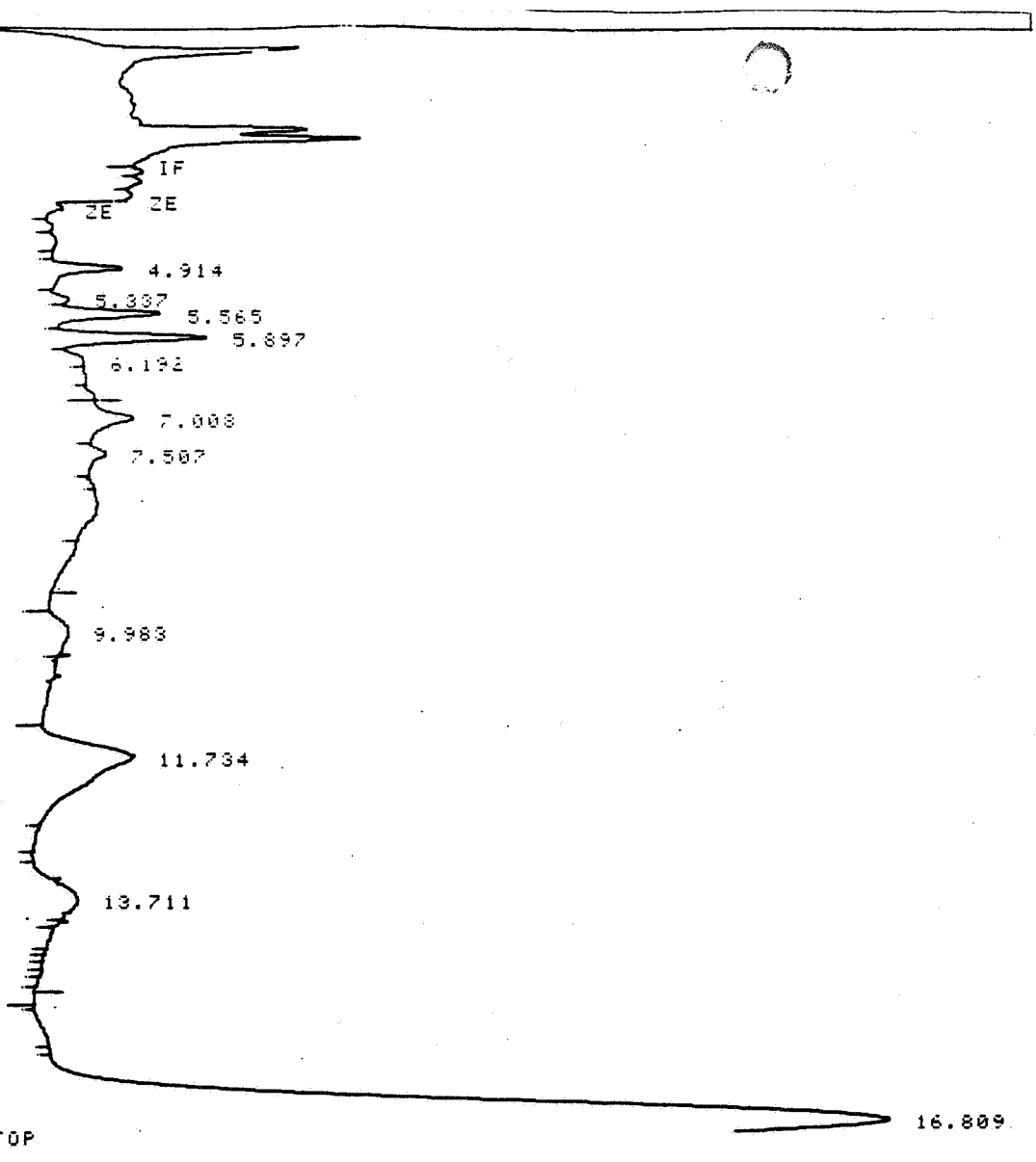
RUN# 253 NOV 25, 1992 13:35:36

SAMPLE NAME: B92-29 SAMPLE# 1
STD. 582H, 0.5UG/ML, 3UL INJ.

B92-29: SAN 582H: DB-17 MEGABORE COL

ESTD-AREA

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	AMOUNT	NAME
5.891	PV	16693	.133	2095	1	.039	SAN 582H



RUN# 255 NOV 25, 1992 14:18:23

SAMPLE NAME: B92-29 SAMPLE# 2
REPEAT CORN FODDER SPIKE, 0.05-1 PPM, SPL.25G-1/4=6.25G/1ML

B92-29; SAN 582H; DB-17 MEGABORE COL

ESTD-AREA

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	AMOUNT	NAME
5.897	PP	7949	.122	1086	1	.018	SAN 582H

TOTAL AREA= 250798
MUL FACTOR=1.0000E+00

RUN # 256 NOV 25, 1992 14:39:45
START