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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, DC 20460

SEP 14 1990

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

OFFICE OF
PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#9F3714, EPA Reg. No. 8340-GI
Fenoxyprop-ethyl in or on Wheat. Amendment of August 21, 1989. Amended Section B and F and Responses to Deficiencies. Request for Method Validation for Proposed Commodities. MRID Nos. 412233-01, 412085-02 and 412086-01. DEB 5828 and 5829.

FROM: Elmer H. Hayes, Chemist
Juan F. Negron, Chemist
Analytical Chemistry Section

THRU: Harvey K. Hundley, Head
Analytical Chemistry Section 9/11/90

THRU: Donald A. Marlow, Chief
Analytical Chemistry Branch

TO: Phil Erico, Head
Dietary Exposure Branch
Health Effects Division

INTRODUCTION

A method trial was requested by the Dietary Exposure Branch, Health Effects Division on the herbicide TILLER, a premix, multiple active ingredient product containing fenoxaprop-ethyl [HOE-33171: ethyl-2-(4-(6-chloro-2-Benzoxazolyloxy)Phenoxy) Proponate] and its metabolites [HOE-53022; 2-(4-(6-chloro-2-benzoxazolyloxy)phenoxy)propanoic acid and HOE-054014; 6-chloro-2,3-dihydrobenzoxazol-2-one] as residues in wheat grain.

The requested fortification levels were 0.05 and 0.10 ppm respectively. Tolerances are established (40 CFR 180.430) for combined residues of the herbicide fluoxaprop-ethyl and its metabolites in or on the raw agricultural commodities, rice, cottonseed, peanuts, peanut shells, and soybeans at 0.05 ppm. The enforcement method for these tolerances (HRAN-1a) was validated by the Environmental Chemistry Laboratory with soybeans as the matrix. (A.E. Dupuy, memo, 9/29/86). It was stated in the description of that method that with modifications it was suitable for use with dry matrices such as rice, soybean, and straw.

The residue data supporting the present tolerance request was generated using Method HRAV-4 that incorporates the modifications and is specifically described for use with wheat grain and straw.

DEB requested that a method validation be conducted using HRAV-4 with wheat grain and wheat straw.

METHOD SUMMARY

Wheat grain is spiked with the specified amounts of fenoxyprop-ethyl or its major metabolites and is then refluxed in a mixture of acetonitrile, hydrochloric acid, and water for six hours. During this process HOE-33171 and HOE-053022 are converted to HOE-054014. The refluxate is diluted with distilled water and filtered to remove undissolved sediment. An aliquot is taken and added to an Extrelut column where co-extractives are eluted with hexane. The hydrolyzed product (HOE 54014) is then eluted with 20% diethyl ether and hexane from the Extrelut column into a round bottom flask and evaporated to dryness on a rotovaporator. The residue is dissolved in ethyl acetate and quantitatively transferred to a test tube where the residue is again evaporated to dryness in a waterbath. The dried residue is then dissolved in a mixture of acetic anhydride/pyridine and derivatized on a heating block apparatus for three hours.

For quantitation the resultant derivative (HOE-083312) is cleaned up using a combination of reverse phase (C_{18}-Sep-Pak) and silica gel chromatography. Final determination was by GLC using an EC detector and employing a megabore, 1.5 um, DB-1, 15 meter x 0.53 mm i.d. column.

COMMENTS

1. The method submitted by the company is well written and easy to follow. However, there are a number of steps that make the method inefficient.

   a. The method is lengthy. Six hours are required to reflux the matrices and six more hours are required from step 6.1.2(d) to step 6.3, not counting steps 6.4 to 6.6 which will add another hour. For gas chromatographic analysis using 40-60 min. per sample analysis time requires a total time of 6-8 hours assuming six samples and three standards are run. Laboratories that do not possess an autosampler would need approximately three days to complete a set of six samples.

   b. A longer hold time on the GLC is suggested as grain interfering extracts vary from commodity to commodity, therefore, it is suggested to hold the GLC at upper temperature for at least 60 minutes.

2. There is interference within the window of interest. A more interference free window is recommended as the general chromatographs of peaks eluted are messy.

3. In section 5.1, there is insufficient direction given about finely grinding the wheat sample. Since the method emphasizes that it is critical that the sample be ground fine, but how fine: very fine, medium fine, coarse fine, flour like? Method should state mesh size for grinding.

4. ACL does not agree with the statement in 6.1.1(d) According to PAM Vol. 1, "Food and Feeds", Section 202.25 stated that wheat grain contains approximately 10% moisture. A 25g sample will result in an equivalent of 2.5 ml of water.

5. The memo from DEB states that standard fenoxyprop-ethyl and its metabolites are available from the EPA repository. Only fenoxyprop-ethyl was in stock. The metabolites need to be acquired from the registrant.

6. ACL used the wheat grain provided by the company, except when the wheat grain was depleted, we used USDA FGIS's wheat grain.

7. Method makes no mention of where one could stop during the day before continuing the next day. Are there critical steps that must remain consistent with the progress?

Commodity Recovery	Chemical Added	PPM Added	PPM Found	% Rec.
Wheat Grain	Control	0.0	N.D.*	
Wheat Grain	Control	0.0	N.D.*	
Wheat Grain	33171	0.05	0.042	84
Wheat Grain	33171	0.05	0.030	60
Wheat Grain	33171	0.10	0.079	79
Wheat Grain	33171	0.10	0.075	76
Wheat Grain	53022	0.05	0.030	60
Wheat Grain	53022	0.05	0.031	62
Wheat Grain	53022	0.10	0.050	50
Wheat Grain	53022	0.10	0.056	56
Wheat Grain	54014	0.05	0.039	79
Wheat Grain	54014	0.05	0.038	77
Wheat Grain	54014	0.10	0.079	79
Wheat Grain	54014	0.10	0.067	68

*ND - indicates not detected at limit less than 0.005 ppm

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Modifications to method (major or minor):

None

Special precautions to be taken:

None

Source of analytical reference standards:

Hoechst Celanese Corporation

If derivatized standard is used, give source:

Hoechst Celanese Corporation (HOE-083312)

Instrumentation for quantitation:

HP/GLC-5890

Instrumentation for confirmation:

HP/GLC-5890

If instrument parameters differ from those given in method, list parameters used:

N/A

Commercial sources for any special chemicals or apparatus:

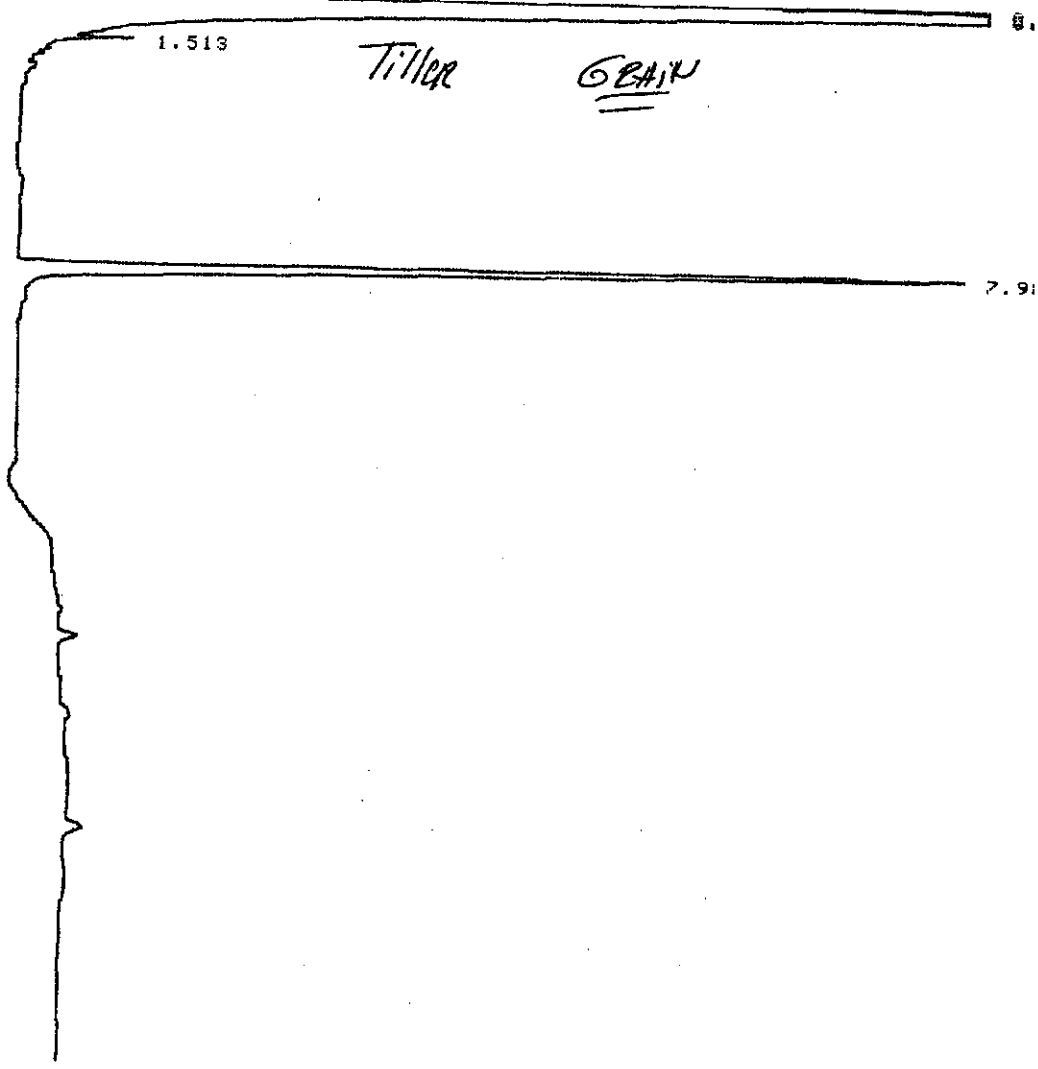
N/A

Additional Comments:

See report.

Chromatograms:

Submitted



RUN# 668 JUL 13, 1990 15:32:42

SAMPLE NAME: HOE33171 SAMPLE# 1
1UL-INJ: .0363UG/ML STTD. HOE83312: B90-18

HEIGHT%

RT	HEIGHT	TYPE	WIDTH	HEIGHT%
.375	90087	PP	.018	3.64915
.479	2363264	PB	.058	95.72858
1.513	977	VB	.045	.03958
7.986	14385	PB	.195	.58269

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MUL FACTOR=1.0000E+00

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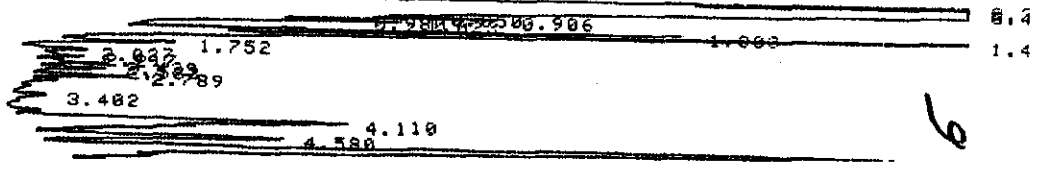

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 SIGNAL 2 = B
  RANGE = 0
  ZERO  = 30.0
  ATTN  = 0

 DETECTOR A = NPD  (OFF)
 DETECTOR B = ECD  (ON)

 PURGE A   = OFF
 PURGE B   = OFF
```

GRAIN Control (25g sample)

```
*  SEQ  START

RUN #  324      JUN 19, 1990  06:40:19
START
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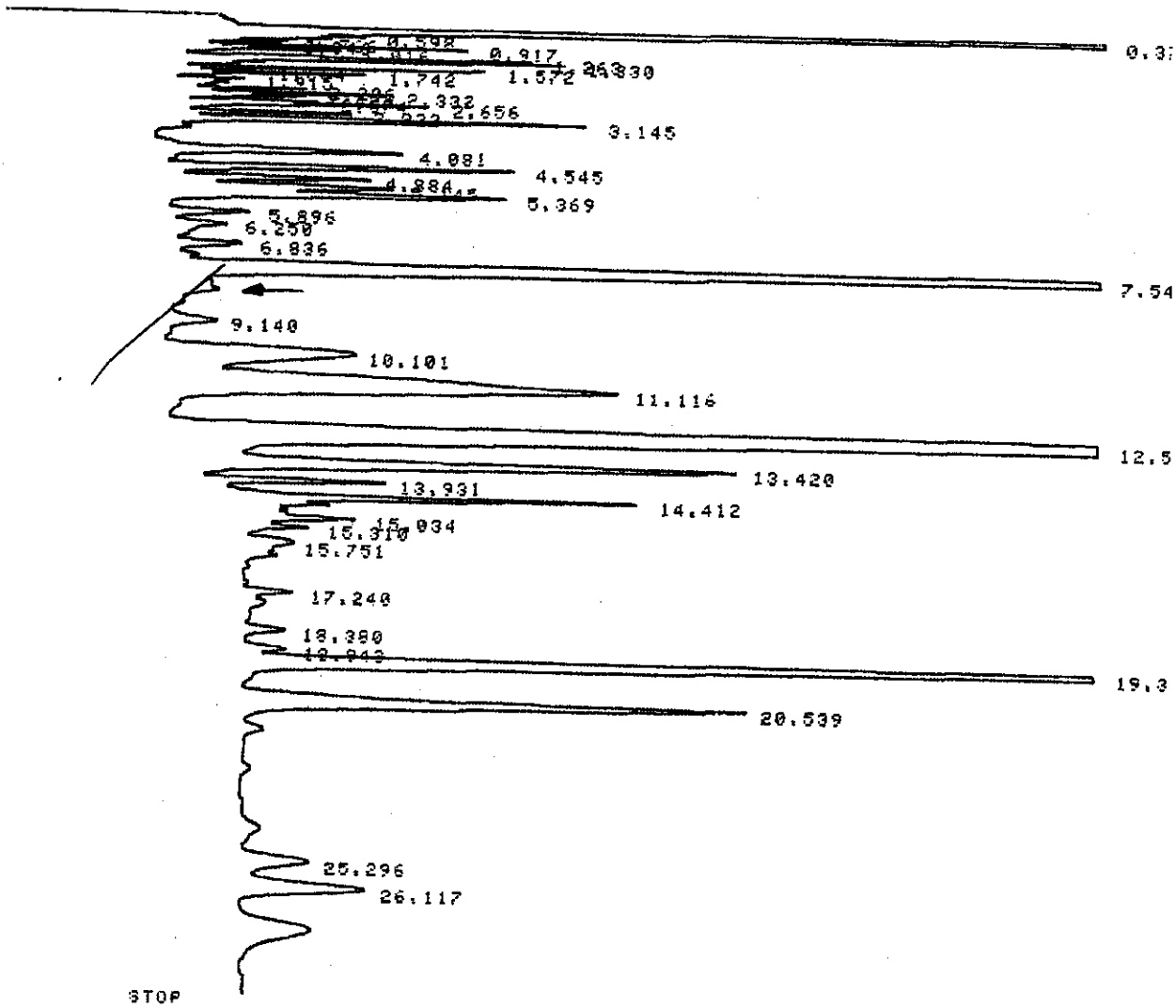


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RUN#    324          JUN 19, 1990  06:40:19

SAMPLE NAME: HOE530[illegible]2          SAMPLE#     1
IUL-INJ:C-2:B90-19

NO CALIB PEAKS FOUND
HEIGHT%
      RT     HEIGHT TYPE  WIDTH     HEIGHT%
```

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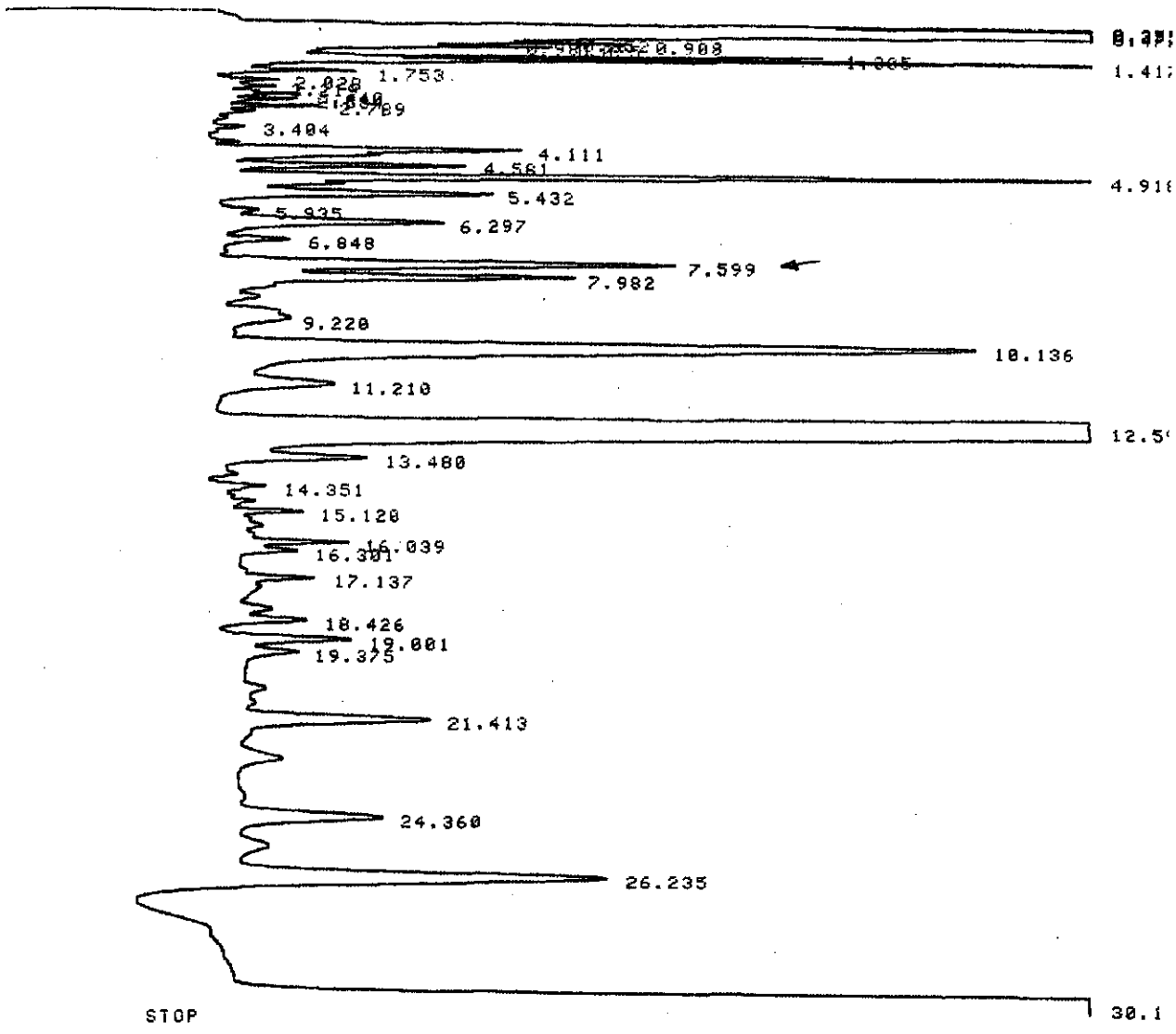

RUN# 670 JUL 13, 1990 16:39:04

SAMPLE NAME: HOE33171 SAMPLE# 2

1UL-INJ: .05-1,FINAL VOL.=2ML: B90-18,SPIKE WITH E.P.A. STD. HOE83312

ppm

HEIGHT%

RT	HEIGHT	TYPE	WIDTH	HEIGHT%
.355	68874	PV	.017	2.54391
.375	71233	VP	.022	2.63104
.477	2271365	PB	.057	83.89446
.852	947	BV	.030	.03498
.908	2745	VV	.038	.10139
.981	1411	VV	.029	.05212
1.025	2709	VP	.036	.10006
1.305	8666	VV	.054	.32009
1.417	36332	VB	.050	1.34195
1.753	1996	BP	.077	.07372
2.028	1029	PV	.095	.03801
2.219	1004	VV	.118	.03708
2.440	1409	VV	.089	.05204
2.584	1377	VV	.099	.05086
2.789	1746	VV	.085	.06449
3.404	585	VB	.139	.02161
4.111	5105	VV	.147	.18856
4.581	4121	VV	.133	.15221

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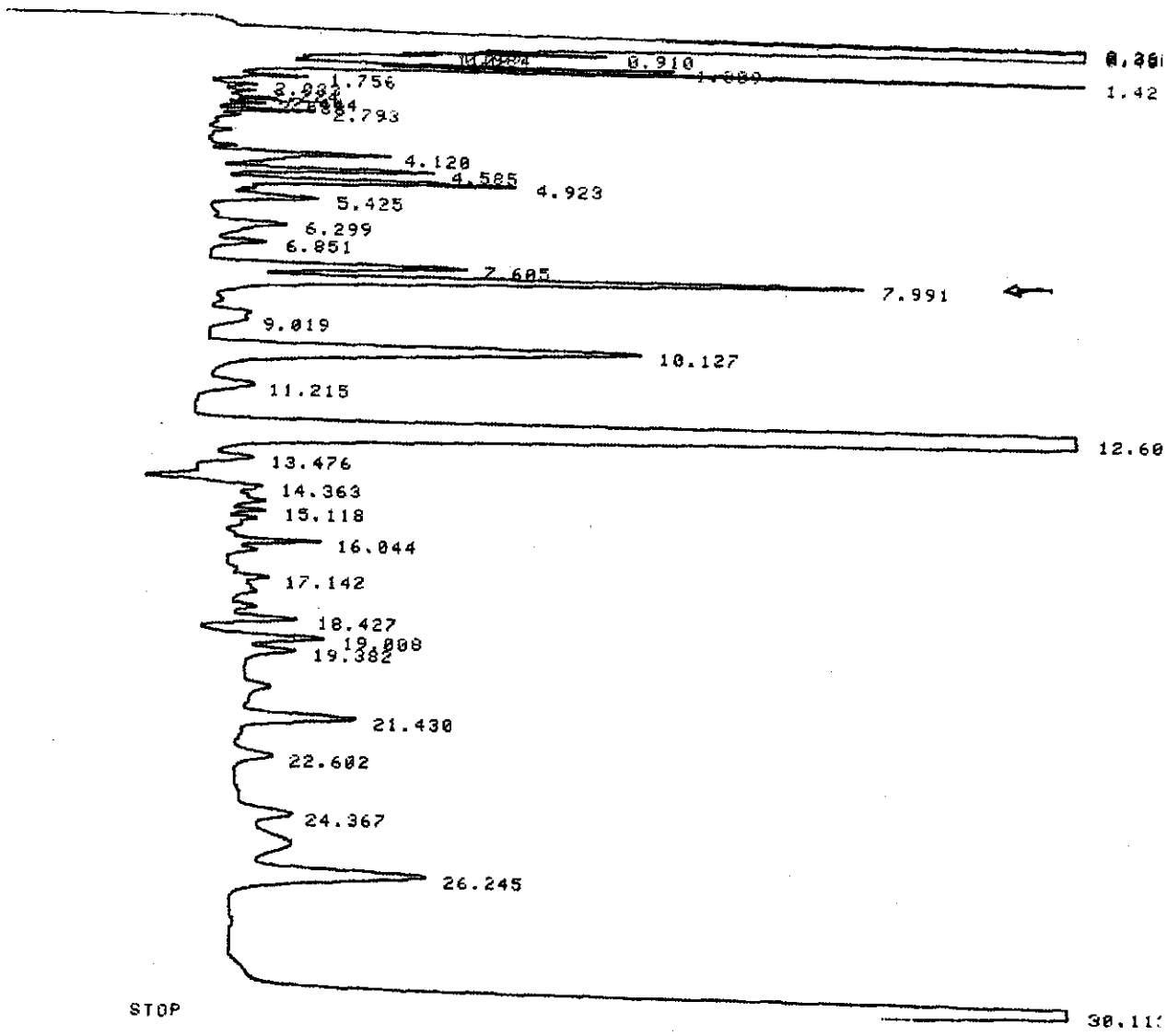

RUN# 675 JUL 13, 1990 19:24:58

SAMPLE NAME: HOE33171 SAMPLE# 5
1UL-INJ: .1-1,FINALL VOL.=2ML; SPIKE WITH E.P.A. STD.HOE33171;B90-18
ppm

HEIGHT%

RT	HEIGHT	TYPE	WIDTH	HEIGHT%
.360	63335	PV	.010	2.48376
.380	65483	VP	.023	2.56800
.480	2249264	PB	.053	88.20762
.910	2875	VP	.037	.11275
.984	931	PV	.028	.03651
1.027	1169	VP	.028	.04584
1.389	6483	BV	.058	.25424
1.421	36893	VB	.049	1.44680
1.756	1316	BP	.076	.05161
2.033	747	PV	.098	.02929
2.224	696	VV	.115	.02729
2.444	1040	VV	.121	.04078
2.588	843	VV	.083	.03306
2.793	1608	VV	.076	.06306
4.120	2971	VV	.203	.11651
4.585	3707	VV	.131	.14537
4.923	5071	VV	.143	.19887
5.425	1768	VB	.197	.06933

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2.019	1745	PV	.081	.06859
2.439	1062	VV	.087	.04181
2.582	1125	VV	.085	.04429
2.789	1778	VV	.090	.06999
3.409	605	VB	.130	.02382
4.109	1666	VV	.176	.06558
4.579	2080	VV	.131	.08188
4.918	2709	VV	.158	.10664
5.380	2265	VB	.180	.08916
6.253	789	PB	.174	.03106
7.594	4763	PV	.227	.18750
7.978	11348	VB	.286	.44672
9.199	2128	BV	.341	.08377
10.116	4427	VV	.346	.17427
11.202	1767	VB	.329	.06956
12.589	31746	BV	.352	1.24969
13.480	998	VB	.240	.03929
14.345	2116	BV	.517	.08330
16.042	858	PV	.443	.03378
18.999	2246	PV	.282	.08841
19.372	1256	VB	.341	.04944
21.422	1956	BB	.298	.07700
23.805	446	PB	.336	.01756
24.330	1016	BP	.307	.04000
25.239	455	PB	.341	.01791
26.209	2612	BB	.425	.10282
30.075	13312 I	BH	.438	.52403

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MUL FACTOR=1.0000E+00

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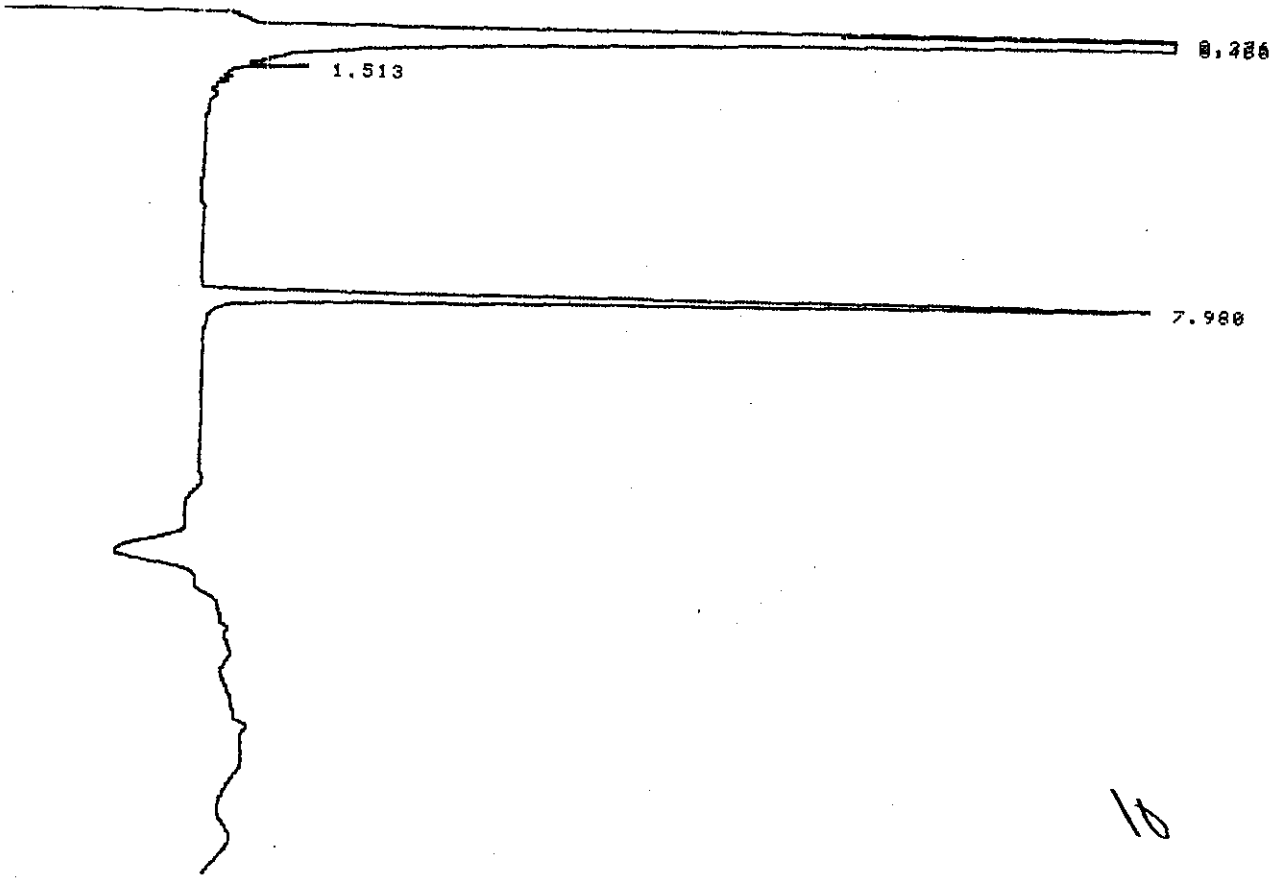


RUN# 690 JUL 17, 1990 17:00:02

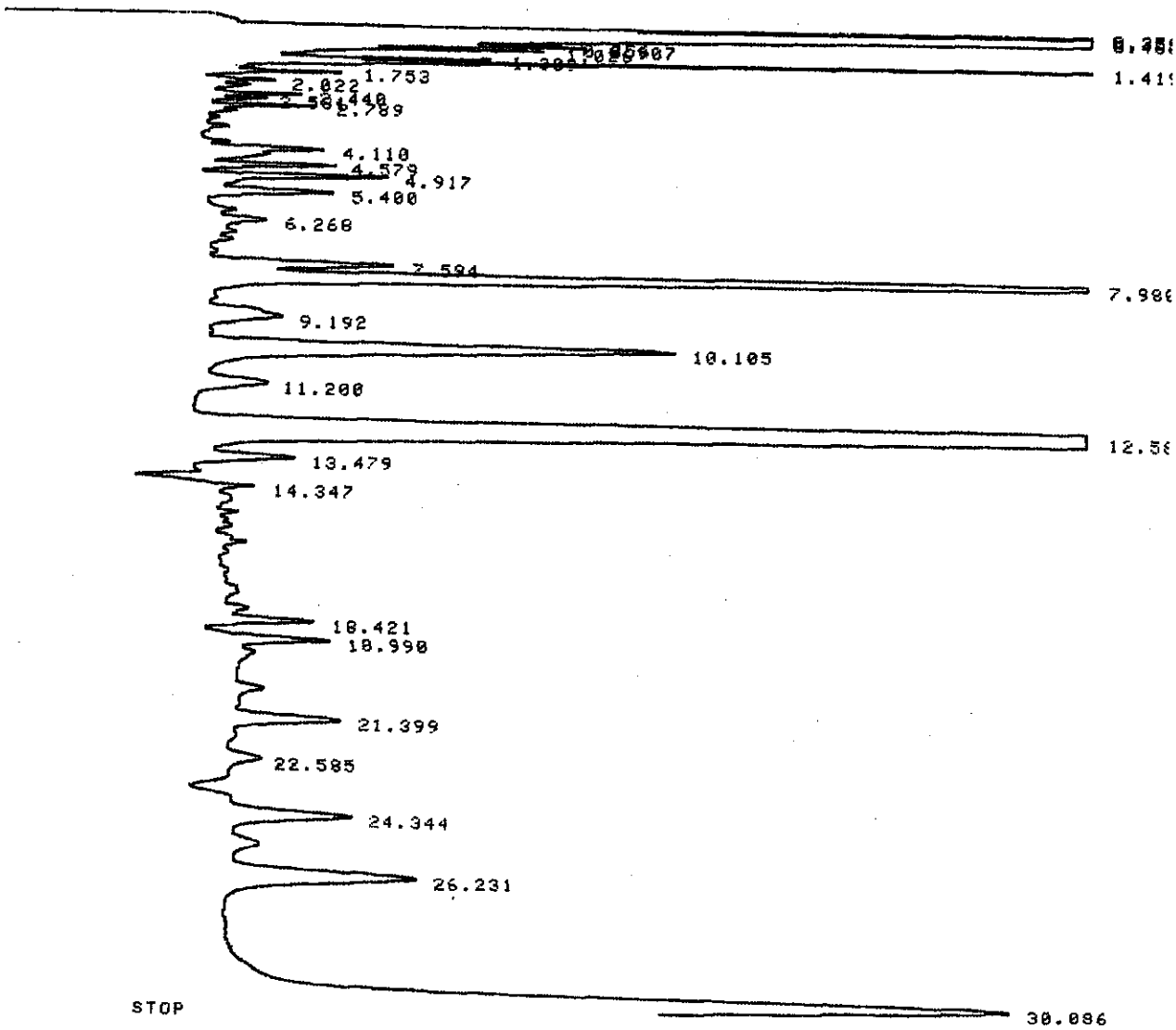
SAMPLE NAME: 54014HOE SAMPLE# 4
1UL-INJ:.0363UG/ML STD. HOE83312:B90-18

HEIGHT%

RT	HEIGHT	TYPE	WIDTH	HEIGHT%
.377	86736	PP	.025	3.50928
.480	2369677	PB	.055	95.87555
1.514	971	VB	.044	.03929
7.978	14234	BB	.195	.57590

TOTAL HEIGHT=2471618
MUL FACTOR=1.0000E+00

RUN # 691 JUL 17, 1990 17:33:15
START



RUN# 691 JUL 17, 1990 17:33:15

SAMPLE NAME: 54014HOE SAMPLE# 5
1UL-INJ:.1-1 FINAL VOL.=2ML:B90-16:SPIKE WITH 54014HOE

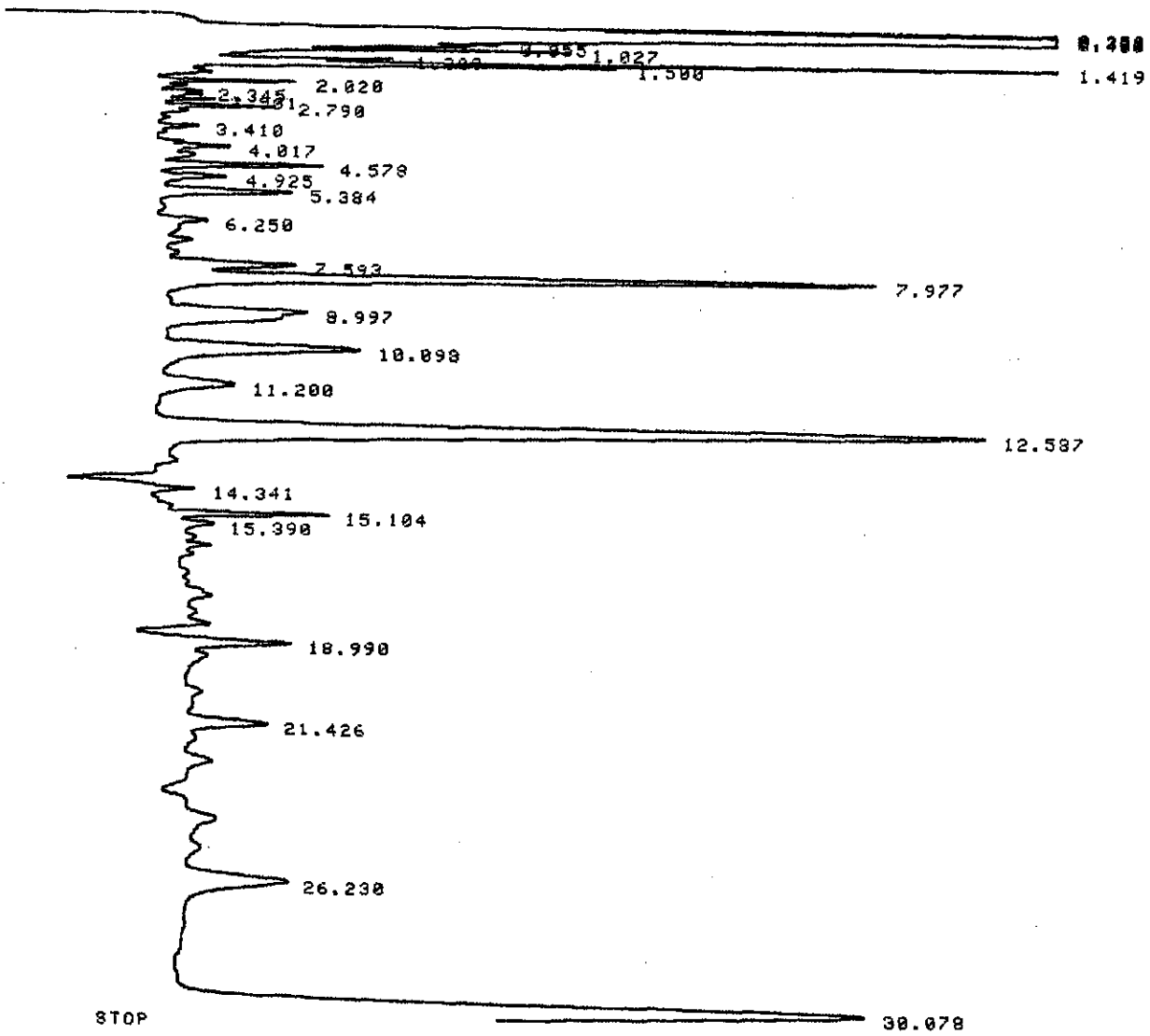
HEIGHT%

RT	HEIGHT	TYPE	WIDTH	HEIGHT%

.378	88197	PP	.037	3.57903
.481	2361322	PB	.055	95.82234
1.514	966	VB	.047	.03920
7.983	13786	PB	.196	.55944

OTAL HEIGHT=2464270
UL FACTOR=1.0000E+00

UN # 685 JUL 17, 1990 14:14:11
TART



UN# 685 JUL 17, 1990 14:14:11

AMPLE NAME: 54014HOE SAMPLE# 2
UL-INJ:.05-1 FINAL VOL.=2ML;B90-18;SPIKE WITH 54014HOE

EIGHT%

RT	HEIGHT	TYPE	WIDTH	HEIGHT%
.359	67345	PV	.021	2.69813
.380	67928	VP	.023	2.72148
.480	2250725	PB	.053	90.17360
.855	1425	BV	.035	.05709
1.027	4551	PB	.035	.18233
1.308	2889	PV	.065	.11575
1.419	25422	VV	.007	1.01854

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SAMPLE NANE: 53022HOE SAMPLE# 7
IUL-INJ:.00: .0363UG/ML STD. HOE83312:B90-10

HEIGHT%

RT	HEIGHT	TYPE	WIDTH	HEIGHT%
8.004	14032	BB	.195	100.00000

TOTAL HEIGHT= 14032
MUL FACTOR=1.0000E+00

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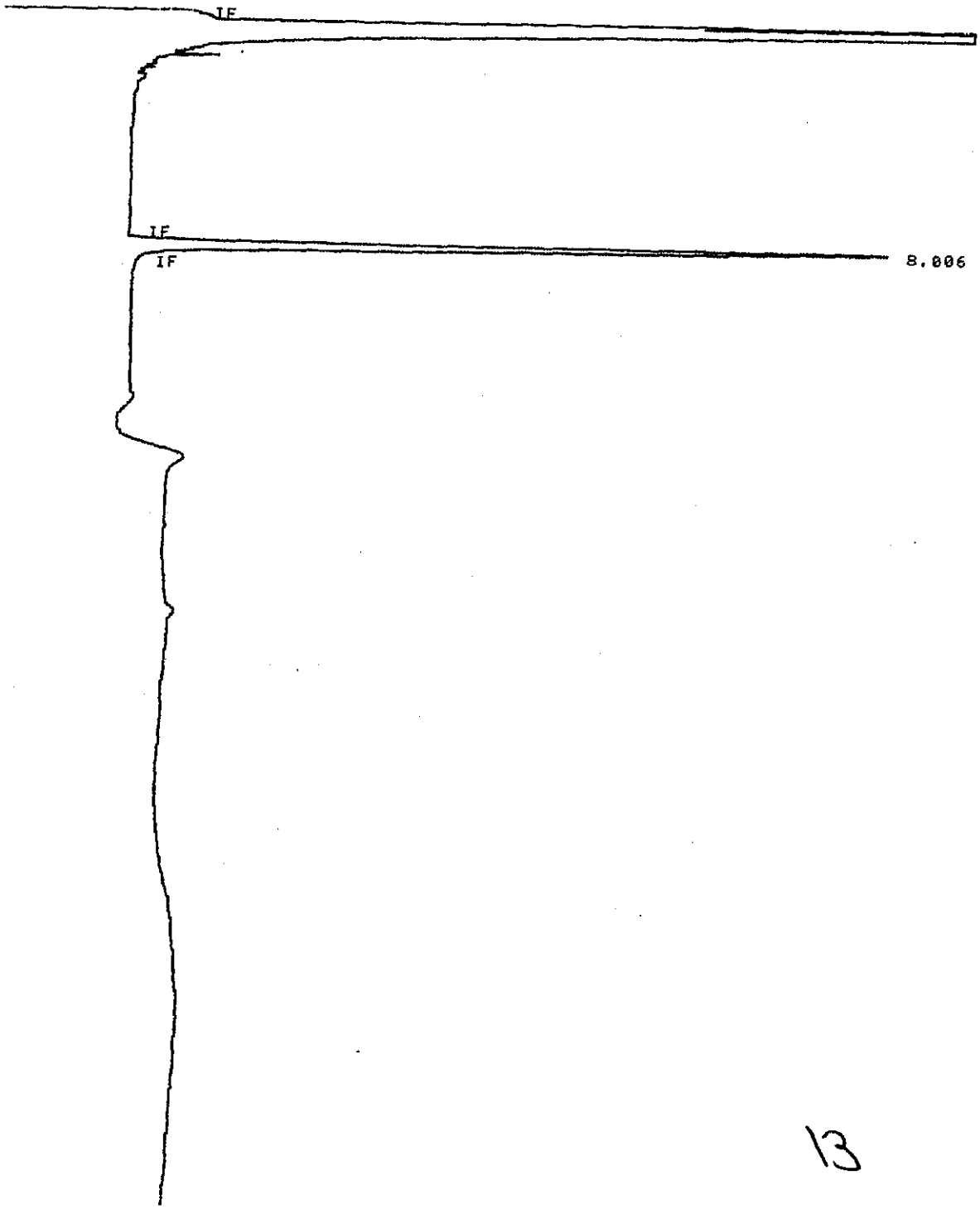
START



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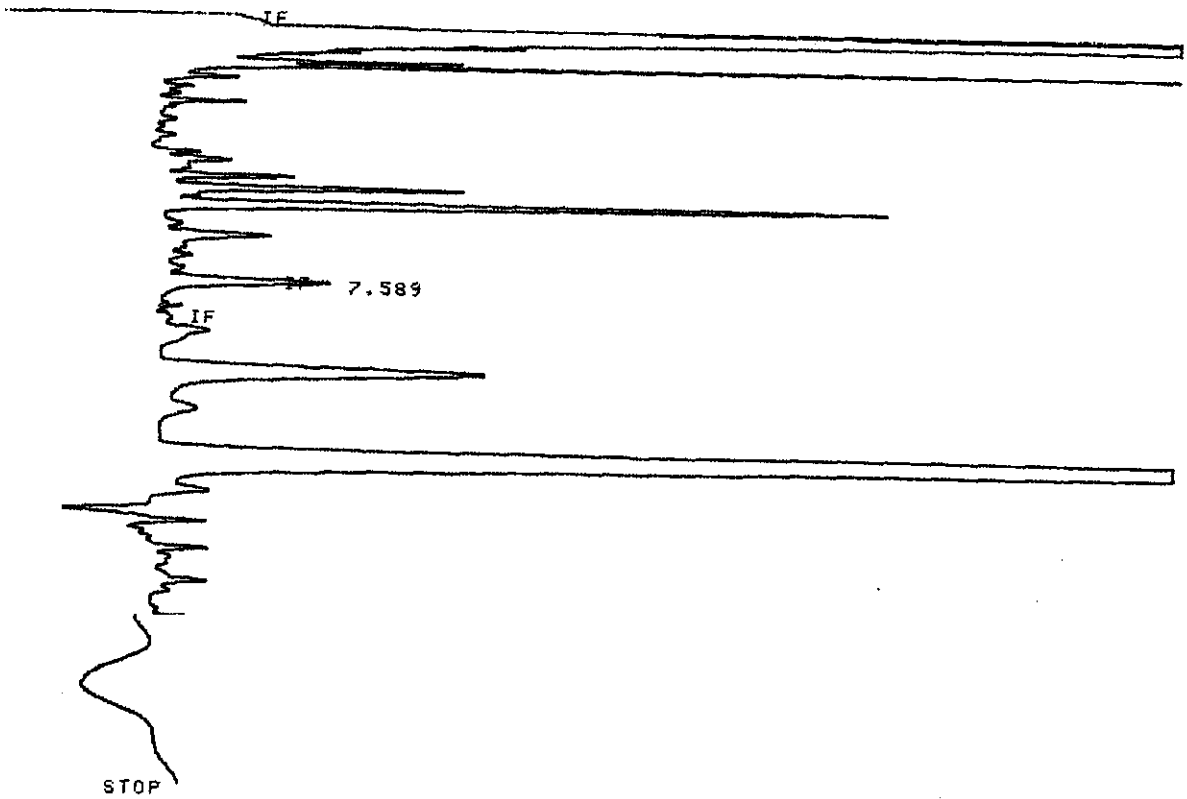
RUN # 768 JUL 25, 1990 15:37:32
START



RUN# 768 JUL 25, 1990 15:37:32

SAMPLE NAME: 53022H0E SAMPLE# 2
1UL-INJ;C-1 WHEAT GRAIN FINAL VOOL.=2ML;B90-10

NO RUN PEAKS STORED

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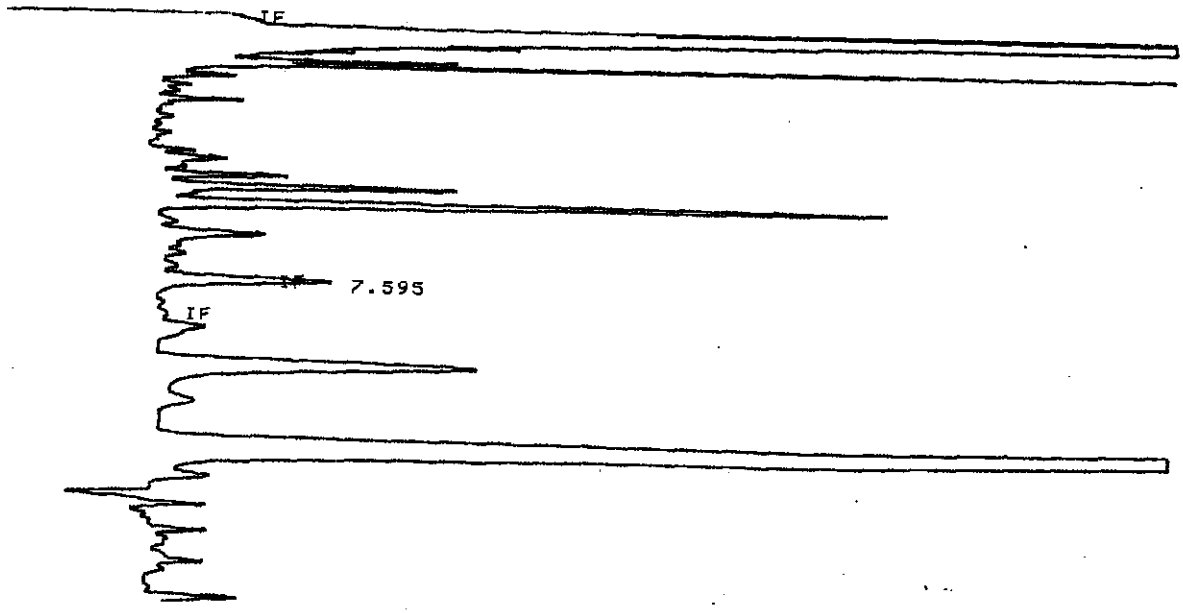
START



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