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Co-Firing High Sulfur Coal with Refuse Derived Fuels

Technical Progress Report #3

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Wei-Ping Pan, John T. Riley and William G. Lloyd

**Center for Coal Science
and
Department of Chemistry
Western Kentucky University
Bowling Green, KY 42101**

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1. Summary

The TG-FTIR-MS system was used to identify molecular chlorine, along with HCl, CO, CO₂, H₂O, and various hydrocarbons in the gaseous products of the combustion of PVC resin in air. This is a significant finding that will lead us to examine this combustion step further to look for the formation of chlorinated organic compounds. The combination of TG-FTIR and TG-MS offers complementary techniques for the detection and identification of combustion products from coals, PVC, cellulose, shredded newspaper, and various blends of these materials.

The pilot atmospheric fluidized bed combustor (AFBC) at Western Kentucky University has been tested. The main purpose of these preliminary AFBC runs were to determine the compatibility of coal and pelletized wood in blends and to explore the effects of flue/air ratio. Our objective is to conduct AFBC burns with 90 percent sulfur capture and more than 96% combustion efficiency.

2. Studies with TGA / FTIR / MS

The raw materials used in this experiment include two bituminous coals, a medium molecular weight PVC resin from the OxyChem Corporation, cellulose from the Whatman Co., and shredded newspaper from Western Kentucky University. In the previous progress report¹ we described the characteristics and behavior of these five materials. We now report on the behavior of various blends of these materials.

The blends were prepared and labelled as follows:

03PVC50 is a mixture of coal 90003 and PVC (50% each)

03NEW50 is a mixture of coal 90003 and newspaper (50% each)

03CEL50 is a mixture of coal 90003 and cellulose (50% each)

03P2N25 is a mixture of coal 90003(50%), PVC (25%) and newspaper (25%)

035122 is a mixture of coal90003 (50%), PVC (10%), newspaper (20%) and cellulose (20%)

Samples 73PVC50, 73NEW50, 73CEL50, 73P2N25 and 735122 are the corresponding blends using coal 92073 in place of coal 90003.

Figure 1 is a schematic of the TGA/FTIR/MS system for this study. A Du Pont 951 Thermogravimetric Analyzer (TG) interfaced to a Perkin Elmer 1650 Fourier Transform Infrared Spectrophotometer (FTIR) was used in this study. The horizontal quartz furnace of the TG was connected to the 10 cm gas cell of the FTIR using an insulated teflon tube heated to a temperature of 150°C with resistance tape controlled by a Powerstat variable auto transformer. The TG was also interfaced to a Fisons Instruments Thermolab Mass

Spectrometer (MS) using a fused silica capillary sampling inlet which is heated to approximately 170°C, Figure 2. A teflon splitter divides the flue gas from TGA into two parts, one to the FTIR (~95%), the other to the MS (~5%).

In the experiments all samples (~100 mg each) were heated in air (50 ml/min) at a rate of 10°C/min to 700°C. The spectra and profiles of gaseous species evolving from the TG system were recorded and analyzed by the TGA-FTIR-MS analytical system.

2.1 Results with TG/DTG

Table 1 is a summary of TG/DTG results for the individual raw materials and for mixtures of the individual components. Compare sample 03PVC50 (50%PVC and 50% coal) with coal 90003 and PVC. It is obvious that the first weight loss is mainly due to the evolution of HCl in PVC. The second weight loss comes from the co-decomposition of coal and PVC.

In sample 03NEW50 (50% newspaper and 50% coal), the first weight loss corresponds to moisture in newspaper, the second weight loss is due to the decomposition of newspaper alone, and the third decomposition stage is due to a second weight loss in coal 90003. It is notable that the weight loss at T_{max} 690°C in newspaper was not observed in the newspaper-coal blends, 03NEW50 and 73NEW50. This may be due to some reactions between coal and the residue of newspaper to form volatile products at a lower temperature. This pattern also occurs with blends using other newsprint stock.

Table 1

Summary of TG/DTG Results

[at 10°C/min to 700°C in air, 50 mL/min flow]

sample	$\Delta W_1(\%)$	T_{\max}	R_{\max}	$\Delta W_2(\%)$	T_{\max}	R_{\max}	$\Delta W_3(\%)$	T_{\max}	R_{\max}
PVC	63.64	317	1.5	10.48	477	0.2	25.88	561	0.4
90003	1.9	80	0.1	89.35	454	1.2			
92073	6.1	80	0.1	69.12	458	0.5			
NEWS ^A	4.57	70	0.2	86.82	346	2.2	2.035	690	0.1
CELL ^A	3.43	60	0.1	96.00	345	5.2			
03PVC50				30.1	307	0.6	64.3	457	0.6
03NEW50	3.23	70	0.1	29.9	340	1.9	59.17	463	0.77
03CEL50	3.8	60	0.1	43.15	341	1.7	48.3	442	1.8
03P2N25	3.2	60	0.1	26.67	302	0.7	64.06	419	1.3
035122	41.21	304	1.0	22.21	420	2.4	19.6	463	1.0
73PVC50				37.7	306	0.7	51.03	437	0.5
73NEW50	4.29	70	0.1	51.02	337	3.3	23.81	444	1.4
73CEL50	4.29	70	0.1	53.41	346	2.3	29.63	423	1.9
73P2N25	30.48	297	1.1	25.81	336	3.1	28.3	432	1.2
735122				66.7	327	5.2	23.56	418	2.1

notes: ΔW is weight loss, in % of original weight

R_{\max} is a maximum rate of weight loss, in weight %/°C

T_{\max} is the temperature at R_{\max} , in °C

^A NEWS is newspaper fiber; CEL is cellulose fiber

2.2 Results with FTIR

2.2.1 Gases Released from Individual Raw Materials

Figures 3-7 show the three dimensional FTIR spectra of the compounds obtained on the combustion of the individual raw materials. The relative axes are absorbance (vertical), wave number (horizontal) and time-temperature (perspective), respectively. The time scale corresponds to the decomposition temperature. The spectra obtained correspond to the TGA thermograms starting at 100°C and with a scan frequency of one per minute.

In coal 90003 and 92073 spectra, a similar trend for decomposition is observed for the CO₂, CO and CH₄ peaks. The peak at 712 cm⁻¹ can be attributed in part to the absorbance of HCN from the decomposition of pyridine structures in coal at 400-670°C. This conclusion can be supported by the double peaks at 3330 and 3280 cm⁻¹ which appear in the same temperature range. However, there are considerable differences between the two spectra. There are more water peaks in coal 90003 than in coal 92073 in the region from 1300 to 1700 cm⁻¹ and 3500 to 4000 cm⁻¹. This can be attributed to more volatile matter and higher hydrogen content in 90003. The COS (2073 cm⁻¹) and SO₂ (1374 cm⁻¹) peaks are stronger for coal 92073 than 90003, reflecting the higher sulfur content. The SO₂ peaks of 92073 provide some evidence about the sulfur forms present. The aliphatic sulfur decomposes first at 300-400°C; then pyrite and thiopene rings decompose at 400-600°C; and finally sulfate salts are predominant at 700-800°C. In coal 92073 spectra, the peaks at 1771 and 1171 cm⁻¹ can be attributed to acetic acid by

comparing their shapes and wave number with standard spectra. The HCl peaks at about 2800 cm^{-1} cannot be identified clearly, even though there is some chlorine content (289 ppm) in coal 92073, owing to masking by the stronger absorption peaks from 3300 to 2500 cm^{-1} .

Another way to present results from the FTIR spectra is to construct evolved gas profiles as shown in Figures 8-10 for coal 90003, PVC, and newspaper, respectively. CO_2 is much more abundant than the other gases released during combustion, and as a consequence must be plotted on a scale different from the other gases. In the PVC evolved gas profile, HCl is released first at $230\text{--}400^\circ\text{C}$, with some CO_2 from the low molecular weight PVC groups. This is in accordance with the TG/DTG results. In the three dimensional graph of PVC (Figure 5), a notable phenomenon is observed at 674 cm^{-1} . The profile at this wave number has two maxima. It is often attributed to absorbance by carbon dioxide. The first maximum, however, is not due to absorbance by CO_2 (no corresponding absorbances at 2356 and $3600\text{--}3700\text{ cm}^{-1}$). From the peaks at 1500 and 3050 cm^{-1} , the first maximum would appear to be due to absorbance by benzene. CH_4 peaks are obvious, while they are not observed in the spectra of newspaper and cellulose. In the spectra for newspaper and cellulose, a number of peaks between $250\text{--}450^\circ\text{C}$ are observed that correspond to the release of water, CO_2 and CO. This reflects the larger oxygen content and OH functionalities in these materials. Also, compared to PVC, many more organic acids (mainly formic and acetic acids) are produced during the combustion of newspaper and cellulose. These can be identified in the three dimensional spectra by groups of peaks at $2500\text{--}3400$ (OH), $1700\text{--}1800$ (C=O), 1033 for methanol, 1106 for formic acid and

1175 cm^{-1} for acetic acid. The appearance of these materials can be attributed to the polyhydroxy structures in newspaper and cellulose.

The evolved gas profiles for PVC are quite characteristic. HCl gas is released first and the absorbance reaches its maximum at approximately 320°C. However, combustion of PVC occurs at 570°C, which is shown by the profiles of carbon dioxide and carbon monoxide. This corresponds to the third weight loss in its TG-DTG curve. These results imply that the PVC is not readily flammable due to its chlorine content. In the profiles of newspaper and cellulose, the absorbance curves of carbonyl (C=O) and C-O have the same shape and reach their maxima at about 370°C. This suggests that these two peaks belong to the same compound, for example, formic acid.

Figure 11 is a comparison of methane profiles for the two coals and PVC. It shows that methane forms at about 500°C. As previously mentioned, because of the high oxygen content in newspaper and cellulose, no methane is formed during the combustion of these materials. It is notable (Figure 11) that there is a little methane released from coals between 230°C to 380°C, but not from PVC. The early methane is thought to be that already present in the micropores of coals. The methane peak at around 500°C is produced by the pyrolytic decomposition of the coal matrix and, to a lesser extent, the PVC carbon chain.

The identified characteristic peaks (not including water peaks which appear in every sample) of FTIR spectra for five raw materials are listed in Table 2.

Table 2

Tentative Identification of FTIR peaks from unblended material^A

[TGA offgas from runs at 10°/min to 700°C in air at 50 mL/min]

<u>Compound</u>	<u>Coal</u> <u>90003</u>	<u>Coal</u> <u>92073</u>	<u>PVC</u>	<u>Newspaper</u>	<u>cellulose</u>
CH ₄	3016	3016	3016		
HCl	2798	2798	2798		
CO ₂	2356	2356	2356	2356	2356
CO			1798	1790	1790
			1788	1773	1777
			1776	1747	1746
			1734	1734	1734
			1717	1717	1724
SO ₂	1374	1374			
Acetic acid			1175	1175	1175
Formic acid			1106	1107	1107
Methanol			1036	1033	
Ethylene	950	950	950	950	950
1,3-Butadiene	910		910		
Furan				745	744
Chlorobenzene(?)	740	741	741		
HCN	712	712			
Benzene			674		

^A numbers in this and following tables are absorbance maxima in wavenumbers (cm⁻¹)

2.2.2 Gases Released from Coal 90003 and 92073 Mixtures

Figures 12 and 13 are 3-D graphs for mixtures of coal 90003(50%) with newspaper (50%) and cellulose(50%). They are similar to one another. A substantial amount of water ($3300-4000$ and $1300-1600\text{ cm}^{-1}$) and organic acids ($2800-3000$, $1700-1900$ and $1000-1200\text{ cm}^{-1}$) are released with small amounts of carbon dioxide and carbon monoxide at approximately 320°C ; these reach their maxima at around 340°C . From TGA data, we know that this decomposition stage can be attributed to the decomposition of newspaper and cellulose. Methane ($2900-3200\text{ cm}^{-1}$) and sulfur dioxide (1374 and 1350 cm^{-1}) begin to appear at about 400°C and reach their maxima at 460°C . Emissions at this stage are mostly due to decomposition of coal. Compared to the spectra of newspaper and cellulose individually, the tails of carbon dioxide peaks in their mixtures are obviously lower. This can be related to lower residues in TGA curves of mixtures after 500°C .

Figure 14 is a 3-D graph of 03PVC50. It is almost a combination of those of coal 90003 and PVC. Similar combination graphs are obtained for 03P25N25, 035122 and all coal 92073 mixtures.

The identified characteristic peaks (not including water peaks which appear in every sample) of FTIR spectra for coal 90003 and 92073 mixtures are listed in Tables 3 and 4. Figures 15 - 22 are the spectra of the identified peaks of 735122 and 035122 mixtures.

Table 3

Tentative Identification of FTIR Peaks from Blends of Coal 92073

<u>Compound</u>	<u>73PVC50</u>	<u>73CEL50</u>	<u>73NEW50</u>	<u>73P2N2</u>	<u>735122</u>
CH ₄	3018	3018	3018	3018	3018
HCl	2798	2798	2798	2798	2798
CO ₂	2360	2360	2360	2360	2360
CO	2175	2175	2175	2175	2175
COS	2074	2074	2074	2074	2074
C=O	1700-	1700-	1700-	1700-	1700-
	1800	1800	1800	1800	1800
SO ₂	1374	1374	1374	1374	1374
Ethyl acetate (?)					1245
Acetic acid	1176	1176	1176	1176	1176
Formic acid	1107	1107	1107	1107	1107
Methanol			1036		
Ethylene	950	950			
1,3-Butadiene	910	906		906	906
p-Xylene	793				
CH ₂ Cl ₂ (?)	756	756	756	756	756
Furan		745	745	745	745
Chlorobenzene (?)	741	741	741	741	741
HCN	712	712	712	712	712

Table 4

Tentative Identification of FTIR Peaks from Blends of Coal 90003

<u>Compound</u>	<u>03PVC50</u>	<u>03CEL50</u>	<u>03NEW50</u>	<u>03PO2N2</u>	<u>035122</u>
CH ₄	3018	3018	3018	3018	3018
HCl	2798	2798	2798	2798	2798
CO ₂	2360	2360	2360	2360	2360
CO	2175	2175	2175	2175	2175
COS	2074	2074	2074	2074	2074
C=O	1700-	1700-	1700-	1700-	1700-
	1800	1800	1800	1800	1800
SO ₂	1374	1374	1374	1374	1374
Acetic acid	1176	1176	1176	1176	1176
Formic acid		1107	1107	1107	1107
Methanol		1033	1036	1033	1033
Ethylene	950			950	950
1,3-Buradiene	910				
CH ₂ Cl ₂ (?)	756	756	756	756	756
Furan		745	745	745	745
Chlorobenzene (?)	741	741	741	741	741
HCN	712	712	712	712	712

2.3 Results with TGA/MS

The Thermolab Gas Analyzer is a low-range, low-sensitivity quadrupole mass spectrometer. As it analyzes mixtures of gaseous molecules which are not subjected to separation techniques, the data obtained requires great care in interpretation. Nevertheless, some useful information can be obtained, especially in conjunction with other sources of structural information, such as FTIR spectra. The MS spectra were collected as the sample in the TGA furnace was being heated.

Figure 23 is a mass spectrum at scan 26 of the offgas of coal 92073, and Figure 24 is the profile of some of the peaks of coal 92073. From Figure 23, the profiles of peaks M/Z 18, 32, 44, 60 and 64 can be attributed to the H_2O , O_2 , CO , COS and SO_2 , respectively. The water profile shows three peaks. The first peak, at around 100°C , is the free moisture in the coal. The second and third peaks are produced due to the combustion and decomposition of coal. The oxygen profile remains stable up to about 350°C , after which it decreases due to its consumption by combustion of the coal matrix. The inverse peak indicates a maximum consumption of oxygen. In addition, sulfur dioxide shows three peaks. This result is the same as that obtained in the FTIR spectra. In 92073, carbonyl sulfide is very obvious and SO_2 shows three decomposition zones.

Figures 25 and 26 show some mass peak profiles for PVC. The M/Z 36 and 38 are formed at the same time over a range of 200 to 450°C and indicate the isotopes H^{35}Cl and H^{37}Cl . Also, the M/Z 70, 72 and 74 peaks suggest the isotopes $^{35}\text{Cl}_2$, $^{35}\text{Cl}^{37}\text{Cl}$ and $^{37}\text{Cl}_2$. These assignments are supported by the ratios of their intensities. The ratio of M/Z 38 to M/Z 36 is 0.333, which is close to the chlorine isotope fraction 0.325. Furthermore, M/Z

M/Z 70 to 72 to 74 appear at exactly the same point, with mass ratio 1.00 : 0.663 : 0.26, as compared with the predicted mass ratio of 1.00 : 0.65 : 0.11. This confirms earlier indications of the formation of Cl_2 via the Deacon reaction.¹ The major aromatic volatile components, benzene (M/Z 78), toluene (92), styrene (104) and indene (116) and their derivatives evidently form at the second decomposition step at 420-460°C.²

Figures 27-36 show mass spectra of the mixtures at specific scans. It is difficult to clearly decipher these complicated spectra. However, we can use FTIR data as a second set of clues and concentrate our attention on the sulfur and chlorine species in the evolved gases.

Figures 37-42 are profiles for the peaks, 36, 38, 70, 72 and 74, for six different PVC-containing blends. All of these show similar trends as that observed in PVC, that is, mass spectrometric evidence that Cl_2 is produced concurrently with the strong HCl release.

Figures 43 and 44 are profiles of peak 112 in spectra 735122 and 035122. The temperature at which it is evolved ($\sim 320^\circ\text{C}$) is the same as that of the peak at M/E 36. This is suggestive of a relationship with the chlorine species, for example, chlorobenzene. In the FTIR spectra, the observed peak at 741 cm^{-1} , matching that of chlorobenzene, appears in the spectra of all of the blends except those of newspaper and cellulose.

Figures 45 and 46 are profiles of the M/Z 60 signal (attributed to both COS and acetic acid), and 64(SO_2) in spectra 035122 and 735122. The peaks are much stronger in 735122 than in 035122. This is due to the higher sulfur content in coal 92073. Also there are three peaks in SO_2 profiles. This is consistent with the profile of coal 92073 and

the FTIR results. For M/Z 60, however, it shows only two peaks in the profile. This may be because after the carbon species is burnt completely, there is enough oxygen to convert the sulfur species into SO_2 and hence the partially oxygenated product COS is not observed.

3. Fluidized Bed Combustion

The pilot atmospheric fluidized bed combustor (AFBC) at Western Kentucky University was built by the University with support from the U.S. Department of Energy. The active bed area is 125 in². The freeboard zone of the combustor is 10 feet high, providing adequate residence time for the combustion of fine fuel particles which may be entrained in the gases leaving the bed. This also allows time for the entrained fine particles of bed material and ash to lose their upward velocity and fall back into the bed, thus minimizing dust loading in the cyclone and providing stable bed height. The fuel is injected into the fluidized bed by using pneumatic injectors. The injectors used for these tests are located about 9" above the air distributor of the combustor. The bed temperature is controlled by fuel feed rate adjustment.

The main purposes of these preliminary AFBC runs are to determine the compatibility of coal and pelletized wood in blends, and to explore the effects of fuel/air ratio. Our objective is to conduct AFBC burns with 90 percent sulfur capture and more than 96% combustion efficiency.

3.1 Burn of April 25, 1995

The first of two tests during this reporting period was made on April 25, 1995, using WKU coal NO.95010, and wood pellets offered by the Jim C. Hamer Co. (Bowling Green, KY).

Characteristics of the coal used are given in Table 5, and those of the wood used are given in Table 6. The combustor operating conditions are listed in Table 7. The fuel

Table 5

Analysis of Coal #95010^A

Moisture (wt %)	2.32%
Ash	7.05
Carbon	77.54
Hydrogen	5.45
Nitrogen	1.59
Sulfur	0.65
Oxygen	7.63
HHV (Btu/lb)	13,750

^A as determined

Table 6

Analysis of Wood Used

Moisture (wt %)	4.71%
Ash	1.09
Carbon	47.56
Hydrogen	6.37
Nitrogen	0.07
Sulfur	0.11
Oxygen	44.73
HHV (Btu/lb)	7,950

Table 7

Combustion Test Matrix

Bed area	125 in ²
Coal/wood feed rate	21-34 lbs/hr
Coal/wood feed size	0.2 x 0 in
Bed temperature	1,500°F [815°C]
Fluidized velocity	3.69 fps
Bed material/sorbent	0.16 x 0 in. limestone

Table 8

Feed Schedule and CO₂ Concentration

<u>Time</u>	<u>Feed Ratio Coal/Wood</u>	<u>CO₂ Concentration (by FTIR)</u>
0900-1325	100% coal	9.9%
1325-1400	79%/21%	10.1%
1400-1440	56%/44%	9.9%
1440-1522	34%/66%	11.1%
1522-1531	14%/86%	11.7%

composition schedule and offgas CO₂ concentration are given in Table 8. Evolved gas was analyzed by gas chromatography (GC) and Fourier Transform infrared spectrometry (FTIR). In addition, gas samples for ion chromatography (IC) and fly ash samples were collected.

During stable combustion, CO and CH₄ disappear, as has also observed from GC analysis. During combustion, we changed the ratio of coal/wood, the results for which are shown in Table 8.

IC was used to measure chloride and sulfate. Gas samples (100 mL) were collected every 15 minutes. IC results are shown in Table 9. Sulfur ranges from 0.73 to 0.95 lbs/MMBtu in coal and wood samples, and the IC data shows that sulfate was not detected, in agreement with FTIR data. Thus limestone appears to be an effective sorbent, absorbing almost all of the sulfur dioxide evolved from the coal and coal/wood combustion. Chlorine is in the range of 1,000 ppm [0.74 lbs/MMBtu] in coal and wood samples, and it is found in the range 0.1-0.5 ppm in IC samples.

The SO₂ lbs/Btu value is calculated as follows.

1. The sulfur content of the coal is 0.65%, and of the wood is 0.11%. If the ratio of coal/wood is 79%/21%, then sulfur in 1 lb of blended fuel is $0.65\% \times 79\% + 0.11\% \times 21\%$, or 0.54%. So 1 lb of blended fuel contains 0.0054 lb. S which can produce 2×0.0054 lbs of SO₂.
2. Similarly, the HHV in 1 lb of 79/21 blended fuel is $13,750 \times 79\% + 7,950 \times 21\%$, or 12,532 Btu/lb.
3. Therefore the SO₂ lb/Btu value $= 0.0054 \text{ lb} \times 2 / 12,532 = 0.86 \text{ lb} / 10^6 \text{ Btu}$.

Table 9

IC Results

<u>Time</u>	<u>Chlorine (ppm)</u> <u>Coal & Wood</u>	<u>IC</u>	<u>SO₂ (lbs/MBtu)</u> <u>Coal & Wood</u>	<u>IC</u>	<u>Experimental Condition</u> <u>ratio of coal/wood</u>
9:15-10:15	1015	0.0	0.95	0.0	100% coal
10:15-10:30	1015	0.155	0.95	0.0	100% coal
10:30-10:45	1015	0.153	0.95	0.0	100% coal
10:45-11:00	1015	0.0	0.95	0.0	100% coal
11:15-11:30	1015	0.248	0.95	0.0	100% coal
11:45-12:00	1015	0.456	0.95	0.0	100% coal
12:30-12:45	1015	0.199	0.95	0.0	100% coal
3:00-13:15	1015	0.172	0.95	0.0	100% coal
13:15-13:30	1015	0.195	0.95	0.0	100% coal
13:30-13:45	951.6	0.195	0.86	0.0	79%/21%
13:45-14:00	951.6	0.147	0.86	0.0	79%/21%
14:00-14:15	882.1	0.151	0.73	0.0	56%/44%
14:15-14:45	882.1	0.0	0.73	0.0	56%/44%
14:45-15:15	815.7	0.0	0.59	0.0	34%/44%
15:15-15:30	755.3	0.0	0.42	0.0	14%/86%

Combustion efficiencies were determined from ash analyses by calculating the amount of carbon burnt, using the following formula:

$$\text{Combustion Efficiency} = \frac{\text{Total Carbon} - \text{Unburned Carbon}}{\text{Total Carbon}}$$

By collecting the fly ash samples. We can analyse the carbon content in the fly ash. The results are listed in Table 10. Combustion efficiencies greater than 97% and frequently around 98%~99% were achieved without employing char recycle. This value of combustion efficiency compares well with values reported elsewhere⁴. The data for coal and wood is also shown in Table 10.

Thermal efficiency is calculated by the thermal balance using the following formula:

$$\text{Thermal Efficiency} = \frac{\text{Exchanged Heat Value}}{\text{Coal and Wood Heat Value}}$$

The thermal efficiency values in Table 11 range from 69.6% to 83.5%. This range of thermal efficiency values for coal and wood compare well with values reported by Dugum and associates³.

3.2 Burn of May 10, 1995

The burn protocols are in general similar to those described above for the burn of April 25, 1995. In this burn, however, only coal was used as fuel, a new gas transfer line (at 1,350°F) was tested, and the air-to-fuel ratio was altered deliberately during the run. Analysis of the coal used (WKU #95011) is shown in Table 12. The experimentally varied conditions are given in Table 13, and the combustor operating conditions in Table 14.

Table 10

Carbon Content in the Fly Ash and Combustion Efficiency

<u>Sample No.</u>	<u>Carbon (%)</u>	<u>Ash (%)</u>	<u>Combustion Efficiency (%)</u>	<u>Ratio of coal/wood</u>
4250930	21.37	76.98	97.5	100% coal
4251000	23.87	74.42	97.1	100% coal
4251030	18.38	80.42	97.9	100% coal
4251100	21.70	76.88	97.4	100% coal
4251130	13.41	84.97	98.6	100% coal
4251200	17.49	81.32	98.0	100% coal
4251230	21.16	77.40	97.5	100% coal
4251300	18.90	79.57	97.8	100% coal
4251330	16.60	82.12	98.2	100% coal
4251400	20.33	78.41	97.9	79%/21%
4251430	15.78	83.10	98.8	56%/44%
4251500	7.84	90.79	99.3	34%/66%
4251540	5.29	93.13	99.8	14%/86%

Table 11

Table 11

Combustion Efficiency

<u>Coal/Wood Wt. (lbs/lbs)</u>	<u>Coal/Wood Wt. Rate (%/%)</u>	<u>Combustion time (min)</u>	<u>Fuel output (Btu/min)</u>	<u>Thermal Efficiency (%)</u>
98.2	100% coal	280	4822.32	69.6
12.2/3.3	79/21	39	4973.97	81.6
8.8/3.3	56/44	36	4862.78	83.5
6.3/12.4	34/66	38	4873.82	83.3
3.4/20.6	14/86	43	4895.81	82.9

Table 12

Analysis of Coal #95011^A

Moisture (wt %)	7.32%
Ash	8.68
Carbon	68.66
Hydrogen	5.53
Nitrogen	1.43
Sulfur	2.97
Oxygen	12.74
HHV (Btu/lb)	12,240

^A as determined

Table 13

Varying the Air to Fuel Ratio

<u>time</u>	<u>ratio of air to fuel (by weight)</u>
8:30-9:00	38.2 : 1
9:00-9:30	25.4 : 1
9:30-10:00	20.7 : 1
10:00-10:30	27.5 : 1
10:30-11:00	31.2 : 1
11:00-11:30	35.5 : 1
11:30-12:00	30.8 : 1
12:00-12:30	27.9 : 1
12:30-13:00	30.7 : 1
13:00-13:30	27.6 : 1
13:30-14:00	20.5 : 1
14:00-14:30	68.9 : 1
14:30-15:00	25.3 : 1

GC results. Again, gas chromatography was used to monitor the principal fixed gases, and it was found that the nitrogen concentration was nearly constant at 70-76%. Moisture did not fluctuate greatly, remaining in the range 8.3-10.8%. CO again appears in the start-up period of unstable combustion, after which it is no longer evident. The reciprocal fluctuations of CO₂ and O₂ as the air/fuel ratio is altered are seen in Figure 50.

Table 14

Combustion Test Matrix

Bed area	125 in ²
Coal feed rate	11.5 to 22 lbs/hr
Coal feed size	0.2 x 0 in
Bed temperature	~1,500°F
Fluidized velocity	2.69 fps
Bed material/sorbent	0.16 x 0 in Limestone

Table 15

Some CO₂ Concentrations (by FTIR)

<u>Time</u>	Port 1		Port 2	
	<u>I</u>	<u>Concn</u>	<u>I</u>	<u>Concn</u>
0928-1004			1365°	10.1%
1008-1027	1015°	7.4%		
1030-1049			1410°	9.4%
1052-1116	1038°	6.2%		
1120-1139			1390°	8.9%

3.3 Discussion

GC was used to measure CO_2 , CO , N_2 , O_2 , H_2O and other gases, and it was found that N_2 concentration was almost constant during the combustion, at 70%~76%, the moisture concentration was also almost constant, ranging from 8.3% to 10.8%. CO occurs in the early period of unstable combustion and briefly when changing the ratio of air/fuel, but once stability is achieved the CO peak disappears, indicating efficient combustion of carbon.

During the combustion, the air / fuel ratio has been deliberately varied (Table 13). To measure the CO_2 concentration, gas samples were collected from two different bed heights [port 1 and port 2 in Table 15].. The concentration of CO_2 at port 2 is higher than that at port 1. But the bed height of port 1 is greater than that of port 2. Theoretically, if there is CO in port 2, there is less CO and more CO_2 in port 1 than in port 2, because CO and O_2 can produce CO_2 as the gases flow upwards. If there is no CO in port 2, the CO_2 concentration in port 1 should be as almost the same as in port 2. The unexpected results (Table 15) suggest a possible air leak between the ports. Corrective modifications are being made.

IC has again been used to measure chloride and sulfate. Every 15 minutes, we collected an IC sample of 100 mL. IC results are shown in Table 16.

The IC data shows that SO_2 was not detected. However, water drops were found on the inside surface of transfer line from the GC outlet to the pump. Based on experience in using TGA-FTIR-MS for analysis in the TA lab., we believe that when moisture in a gas stream condenses into water drops, most of the acid gases HCl and SO_2 dissolve in the

Table 16

IC Results

<u>Time</u>	<u>Chlorine (ppm)</u>		<u>SO₂ (lbs/MBtu)</u>		<u>Ratio of Air/Fuel</u>
	<u>Coal</u>	<u>IC</u>	<u>Coal</u>	<u>IC</u>	
8:45-9:00	24	0.116	4.85	0.0	38.2:1
9:00-9:15	24	0.129	4.85	0.0	25.4:1
9:15-9:30	24	0.0	4.85	0.0	25.4:1
9:30-9:45	24	0.027	4.85	0.0	20.7:1
9:45-10:00	24	0.053	4.85	0.0	20.7:1
10:00-10:15	24	0.101	4.85	0.0	27.5:1
10:15-10:30	24	0.045	4.85	0.0	27.5:1
10:30-10:45	24	0.036	4.85	0.0	31.2:1
10:45-11:00	24	0.037	4.85	0.0	31.2:1
11:00-11:15	24	0.034	4.85	0.0	35.5:1
11:15-11:30	24	0.034	4.85	0.0	35.5:1
11:30-11:45	24	0.078	4.85	0.0	30.8:1
11:45-12:00	24	0.069	4.85	0.0	30.8:1
12:00-12:15	24	0.049	4.85	0.0	27.9:1
12:15-12:30	24	0.043	4.85	0.0	27.9:1
12:30-12:45	24	0.070	4.85	0.0	30.7:1
12:45-13:00	24	0.112	4.85	0.0	30.7:1
13:00-13:15	24	0.108	4.85	0.0	27.6:1
13:15-13:30	24	0.088	4.85	0.0	27.6:1
13:30-13:45	24	0.055	4.85	0.0	20.5:1
14:00-14:15	24	0.046	4.85	0.0	20.5:1
14:15-14:30	24	0.0	4.85	0.0	68.9:1
14:30-14:45	24	0.0	4.85	0.0	68.9:1
14:45-15:00	24	0.067	4.85	0.0	25.3:1
15:00-15:15	24	0.124	4.85	0.0	25.3:1

droplets. Hence these IC results are not a true estimate of chloride and SO_2 . In order to get the correct IC result, we will collect future IC samples at the GC outlet.

During the May 10th burn, the thermal efficiencies were in the range from ~32% to ~59%. The detailed calculation results are listed in Table 17. Compared to the result of April 25th combustion, the thermal efficiencies are lower, because the emphasis this time was variation in the air-to-fuel ratio.

Ratio of Air/Fuel and Bed Temperature. Figure 51 shows that a sharp increase in the air/coal ratio results in a sharp drop in temperature. When the high air/coal ratio is reduced, bed temperature rises sharply.

Combustion Efficiency. Combustion efficiencies were determined, as before, from the ash analyses by calculating the amount of carbon that was burnt.

By collecting the fly ash samples to analyze the carbon content in the fly ash. The results are listed in Table 18. Combustion efficiencies greater than 95% and frequently around 96%~99% were achieved without employing char recycle. This range of combustion efficiency value compares well with values reported elsewhere³. Other data for coal combustion efficiency are presented in Table 11.

3.4 Discussion

Gas chromatography was used to provide semicontinuous measures of CO_2 , CO , N_2 , O_2 , H_2O and other gases in the combustion offgas. N_2 concentration was found to be almost constant during the combustion, at 70%~76%. Moisture content was also almost constant, ranging from 9.5% to 10.3%. CO only occurs in the early unstable combustion

Table 17

Thermal Efficiency

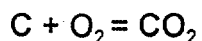
<u>Time</u>	<u>Thermal Efficiency(%)</u>	<u>Ratio of Air/Fuel</u>
08:30-09:00	58.84	38.2:1
09:00-09:30	39.11	25.4:1
09:30-10:00	31.87	20.7:1
10:00-10:30	42.40	27.5:1
10:30-11:00	48.11	31.2:1
11:00-11:30	54.76	35.5:1
11:30-12:00	47.46	30.8:1
12:00-12:30	42.98	27.9:1
12:30-13:00	47.35	30.7:1
13:00-13:30	42.56	27.6:1
13:30-14:00	51.80	20.5:1
14:00-14:30	46.80	68.9:1
14:30-15:00	39.10	25.3:1

Table 18

Carbon Content in the Fly Ash and Combustion Efficiency

<u>Sample No.</u>	<u>Carbon(%)</u>	<u>Ash(%)</u>	<u>Combustion Efficiency(%)</u>	<u>Ratio of Air/Fuel</u>
0510-0900	46.39	53.61	92.49	38.2:1
0510-0930	31.58	68.42	95.99	25.4:1
0510-1000	34.16	65.84	95.50	20.7:1
0510-1030	29.22	70.78	96.42	27.5:1
0510-1100	31.84	68.16	95.95	31.2:1
0510-1130	29.88	70.12	96.30	35.5:1
0510-1200	30.52	69.48	96.19	30.8:1
0510-1230	20.40	79.60	97.78	27.9:1
0510-1300	25.02	74.98	97.10	30.7:1
0510-1330	36.24	63.76	95.07	27.6:1
0510-1400	9.03	90.97	99.14	20.5:1
0510-1430	41.12	58.88	93.94	68.9:1
0510-1500	16.43	83.57	98.29	25.3:1

period. Once stability was achieved, the CO peak disappeared, showing the carbon combustion to be efficient. Figures 47 and 48 show the concentrations of CO₂ and O₂ in two periods of this run. When CO₂ concentration decreases, O₂ concentration increases, and vice versa. Indeed, the sum of CO₂ and O₂ concentrations remains constant. Bed and flue gas temperatures remain throughout in fairly narrow ranges (Figure 49). Thus with excess O₂, at about 1500 °F bed temperature, the main reaction of carbon⁵ is



Owing to the stoichiometry of the above reaction, the molar sum of O₂ and CO₂ is constant.

FTIR was employed to measure CO₂, CO, CH₄, SO₂ and other gases. From FTIR's wavenumber charts, CO and CH₄ can be seen only in the early period of instability.

The bench-scale fluidized bed combustion tests were conducted on a low sulfur (~2.97% sulfur) WKU coal No. 95011 in the WKU fluidized bed. The bed was operated at ~1500 °F at a fluidizing velocity of 2.69 fps. SO₂, CO₂ and other gas emissions were monitored by FTIR.

Summary. The bench-scale fluidized bed combustion tests were conducted on a low sulfur (~0.65% sulfur) WKU coal No. 95010 in the WKU fluidized bed on April 25, 1995. The six-hour burn started with coal, gradually switching to sawdust pellets. The first gas analysis line detected CO₂, SO₂, CO, H₂O, O₂, and N₂ quantitatively. No difficulty was encountered in using a mixture of 95% sawdust and 5% coal to maintain the bed

temperature around 1500 °F. [A plot of bed temperature vs time is shown in Figure 49.]

The fluidizing velocity is 3.69 fps. The results of tests show that:

1. Combustion efficiencies greater than 97 percent were achieved without employing char recycle. Generally, the combustion efficiencies of mixtures of coal and wood were greater than those of pure coal.
2. Thermal efficiencies from 69.6% to 83.5% were realized in each of the tests conducted with all of the fuel blends tested.
3. By using limestone as bed material, sulfur capture of more than 90% was achieved.
4. By employing techniques of IC, GC and FTIR, CO₂, CH₄, CO, SO₂, O₂, N₂, Cl and other gases could be effectively analyzed and quantified.
5. Port 2 works better than Port 1, because we obtain quantitative results for CO₂ and other gases.

4. GC/Mass Spectrometry

In preparation for the identification and proximate quantitation of individual organic compounds formed in the course of coal combustion (task C-3), the Shimadzu QP-5000 GC/Mass Spectrometer has been fully evaluated, using the group of 27 organic compounds most frequently reported as coproducts of coal combustion.¹ An analytical program has been developed (Table 19) which separates each of these compounds, and in addition can distinguish 32 additional suspected product compounds as well as several spiking standards [reference compounds which themselves will not be formed in coal combustion]. The spiking standards are fully deuterated compounds: phenol-d6 [b. 180°C], naphthalene-d8 [b. 218°], phenanthrene-d10 [b. 340°], p-terphenyl-d14 [b. 390°] and chrysene-d12 [b. 448°].

Two compounds, anthracene and phenanthrene, are commonly found in combustion products and are often reported together, since their GC retention times are sometimes indistinguishable and their mass spectra are virtually identical. We have resolved this pair, using a 60-m x 0.32-mm capillary column coated with the polydimethylsiloxane Rtx-1 (Table 19). Each member of this pair has been identified and verified using pure analytes.

When compounds have been identified and their mass spectra determined, the most sensitive way to use the mass spectrometer is in its selected ion monitoring (SIM) mode. SIM runs with this instrument provide both higher signals -- since the instrument is spending most of its time measuring the signals from the principal mass fragments of the targeted compounds -- and also lower background noise. For a group of test

hydrocarbons, the useful threshold sensitivity for integrating peak areas in the scanning mode is ~100 pg. [1 pg = 10^{-12} g.] In the SIM mode using four selected m/e fragments this threshold sensitivity drops to ~ 1 pg.

Table 19

GC/MS Conditions for the Simultaneous Analysis of 65 Compounds

GC	injector	300°	MS	electron multiplier	1.50 kV
	transfer line	290°		commence scan	5.0 min
	column	60m x 0.32mm		mass range	40-400 amu
		Rtx-1, 1.0 μ m		scan rate	4 Hz
	col temp	100° + 5°/min to		integrator width	1 sec
		330°, then isothermal		threshold	100 μ v
	carrier flow	1.50 mL/min throughout			
	lin velocity	31.1 cm sec ⁻¹			

5. Acknowledgments

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Susan Hodgdon

graduate students (chemistry):

Jake Li

Jessica Lin

Richard Lu

Shobha Purushothama

Hongtao Zhang

6. References

1. Pan, W.-P., Riley, J. T., Lloyd, W. G., **Co-firing High Sulfur Coal with Refuse Derived Fuels**, US DOE grant DE-FG22-94PC94211, Techn. Progr. Rept. #2, February 25, 1995, pp 7ff, 13..
2. Lattimer, R. P., Kroenke, W. J., *J. Appl. Polymer Sci.*, **27**, 1355 (1982)
3. Dugum, J. N., and coworkers, *Proc. 8th Intl. Conf. for Underbed and Overbed Feed Systems*, **1985**, 255.
4. Sethi, V. K., Bland, A. E., Snell, G. J., *ibid.*, **1989**, 1211.:
5. Basu, P., "Fluidized Bed Boilers - Design and Application", Pergamon Press, 1983.

7. Figures-

Figure 1. TG-FTIR-MS Analytical System

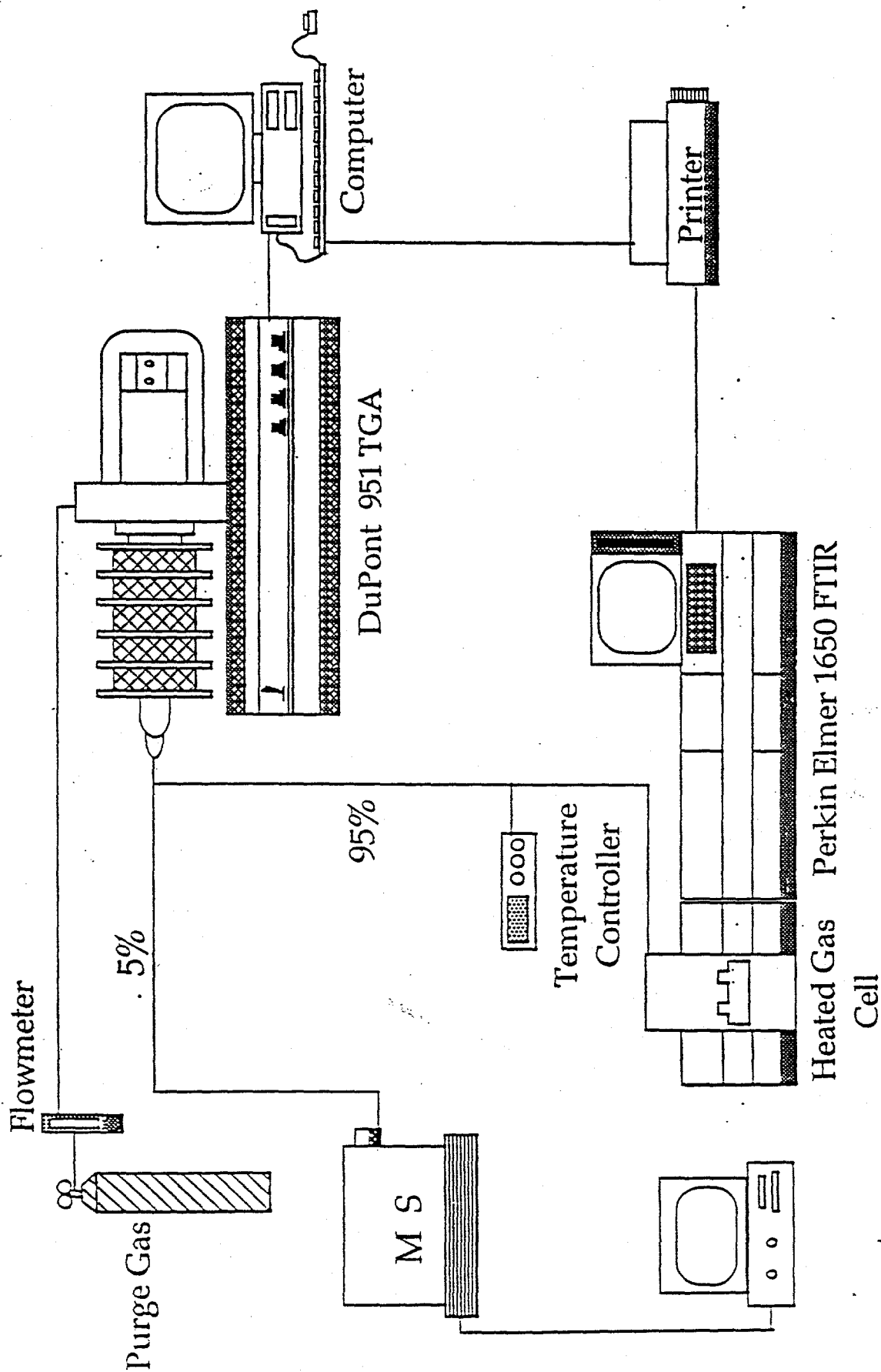


Figure 2. TGA-MS Capillary Interface

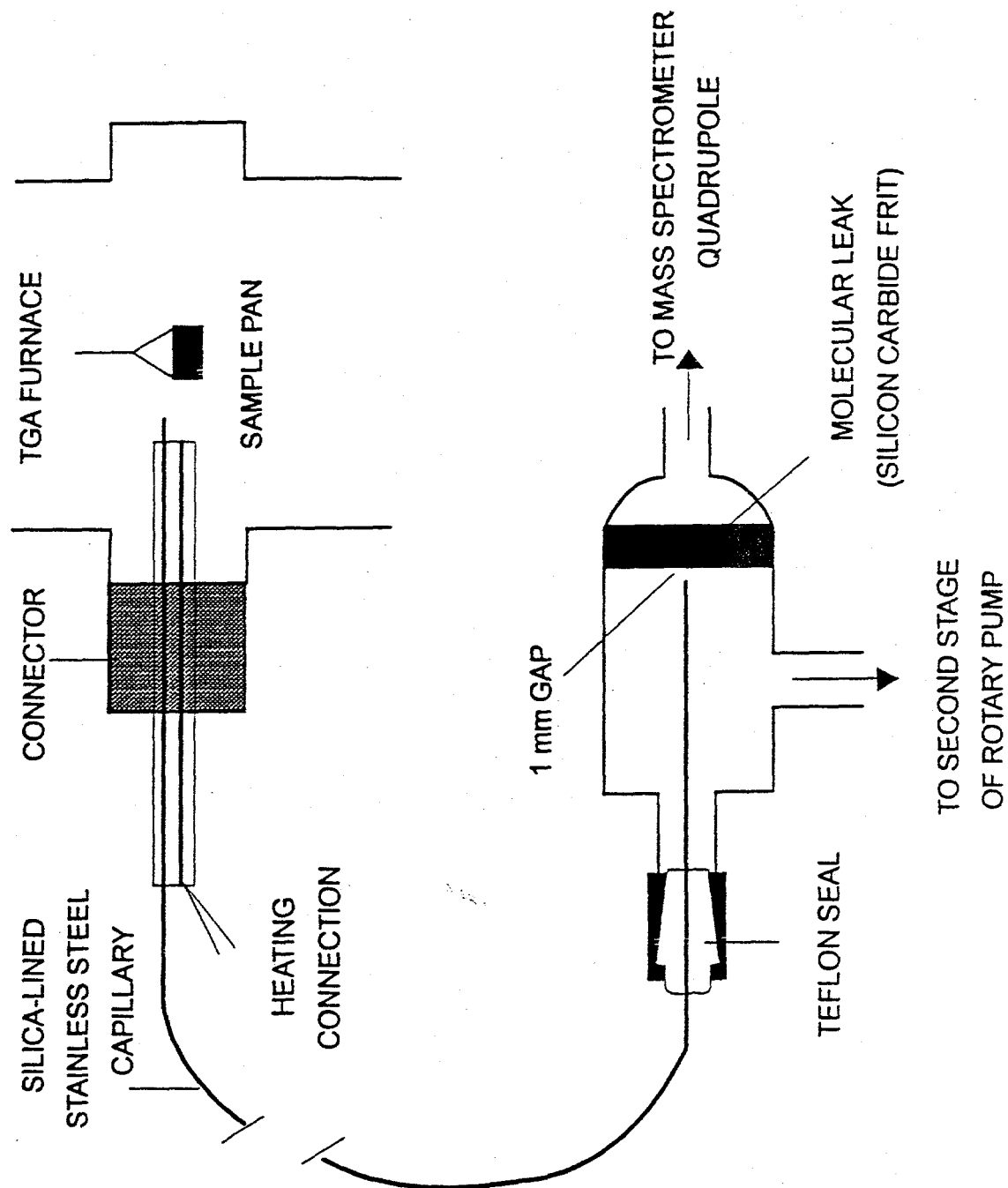
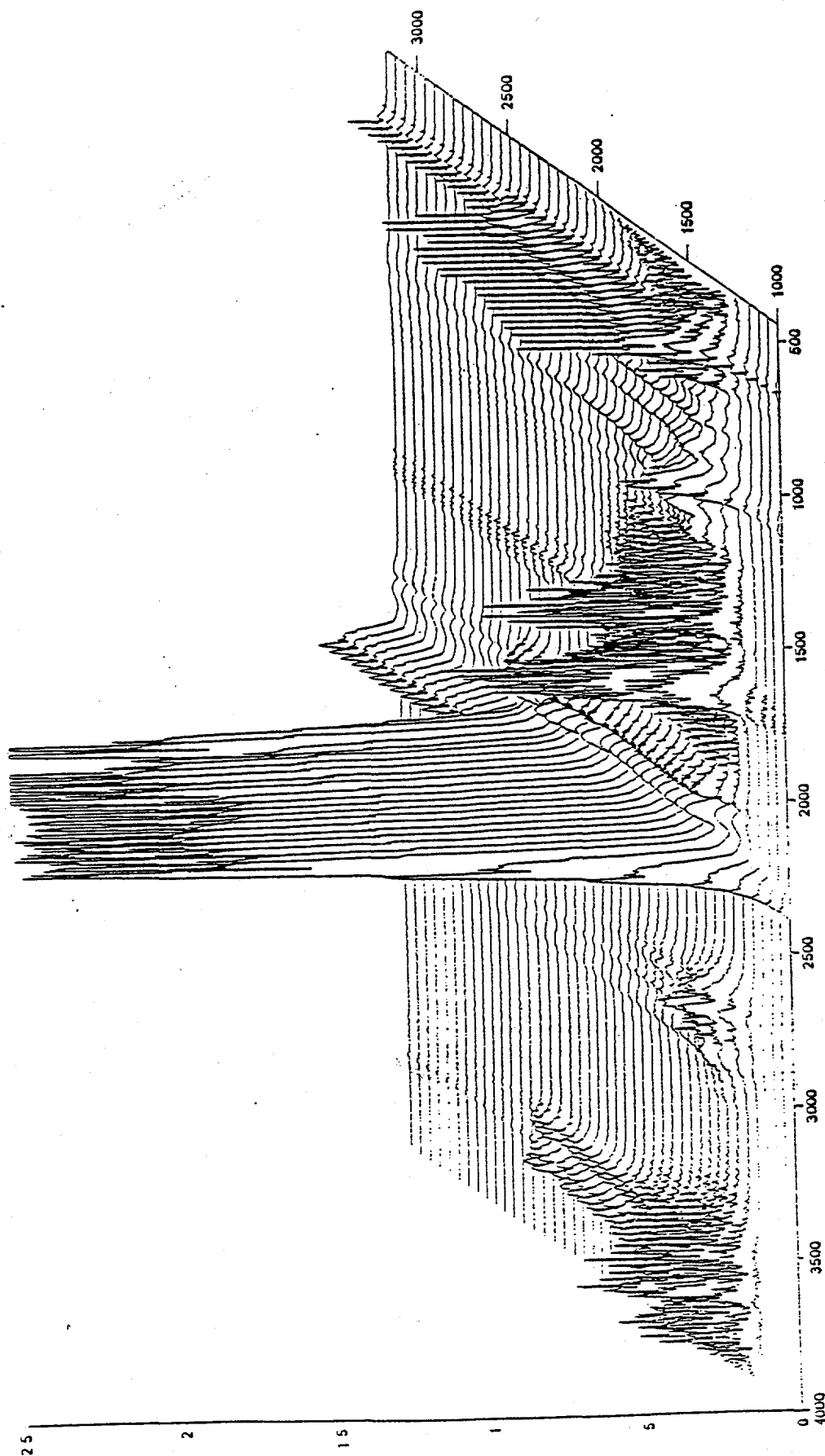


Figure 3. FTIR Spectra of Cellulose



HIDE3D Y-ZOOM CURSOR

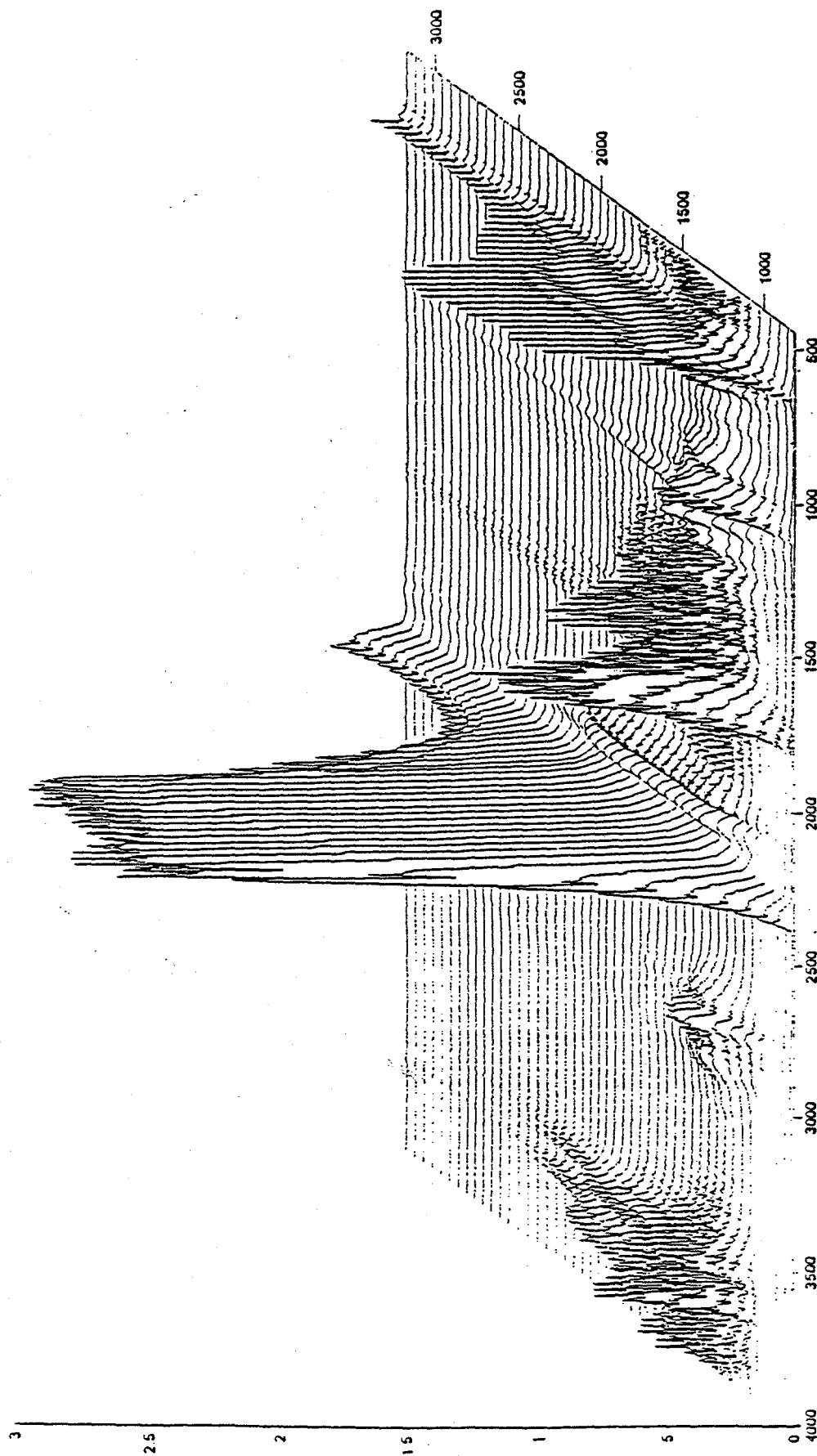
12/21/94 11:39 AM Res=4 cm⁻¹

Absorbance / Wavenumber (cm⁻¹)

File # 1 = CELLULOSE#20 @ 100424

Scanning in air 2000/min, 100/min to 7000

Figure 4. FTIR Spectra of Newspaper



Absorbance / Wavenumber (cm-1)

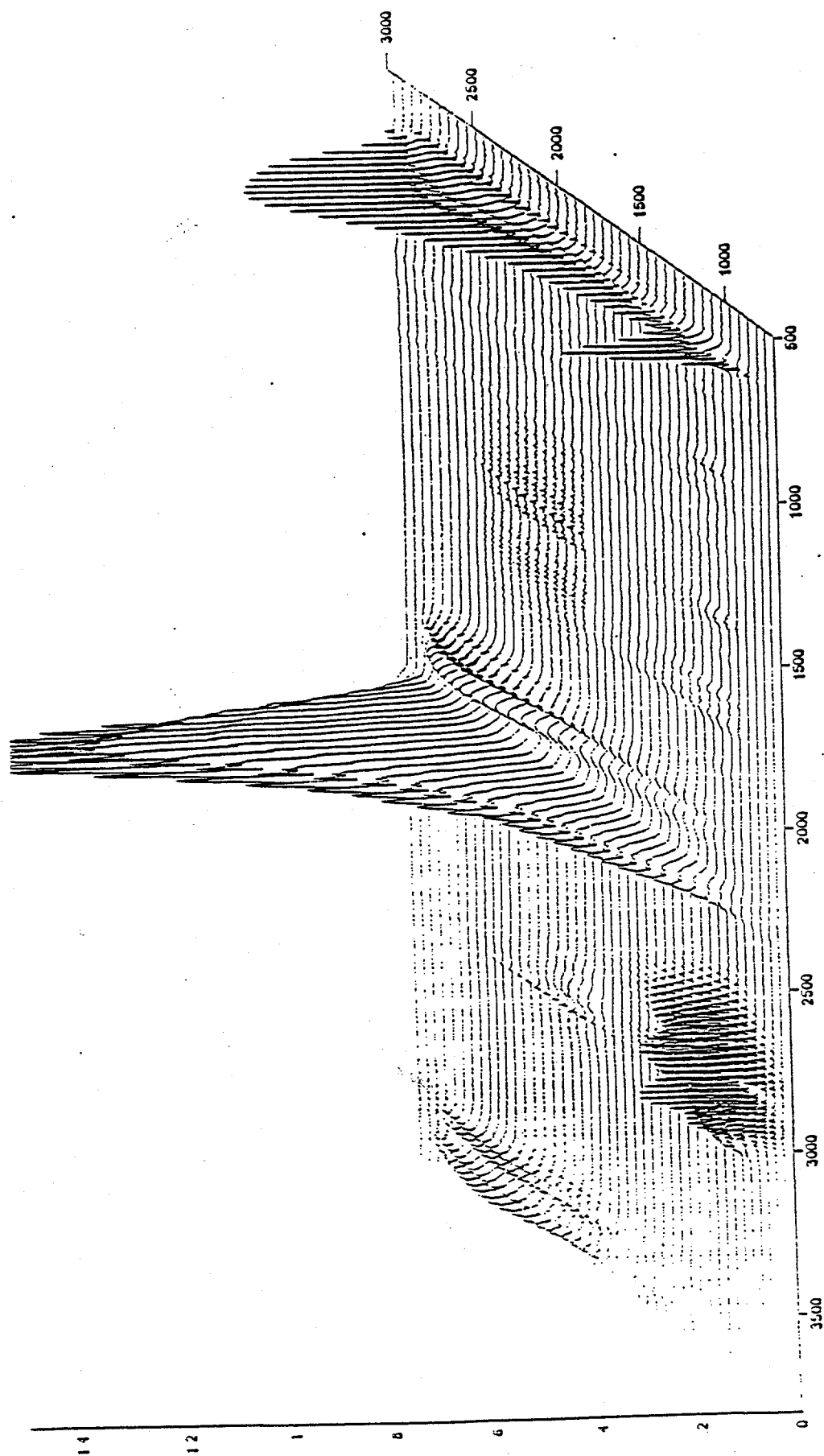
File # 1 = NEWSPAPER#16 @ 793 329

Scanning in air 500/min, 10C/min to 700C

Hide3D Y-Zoom CURSOR

12/21/94 1:37 PM Res=4 cm-1

Figure 5. FTIR Spectra of PVC



Hide3D Y-Zoom CURSOR

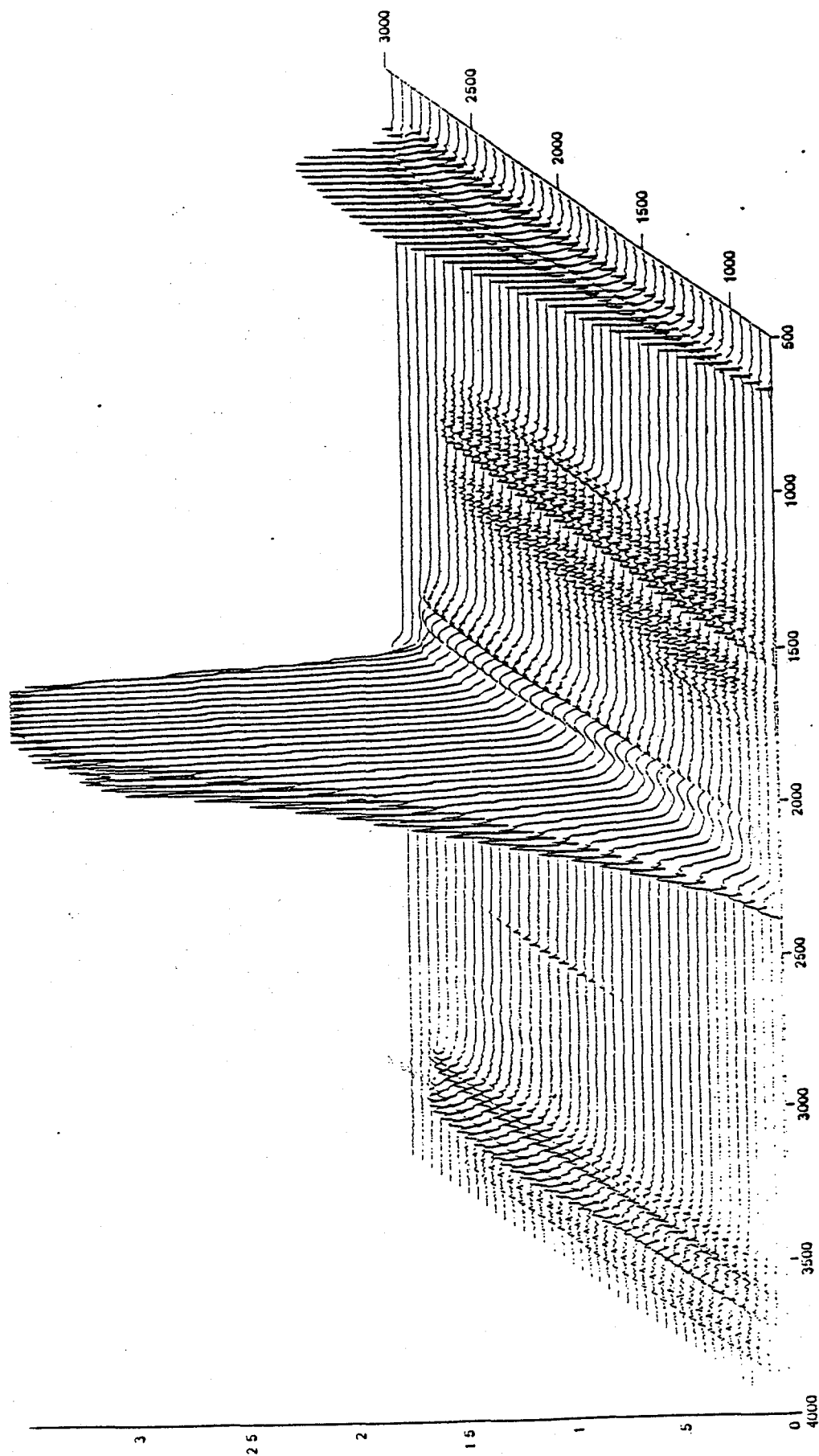
11/27/94 10:00 AM Res=4 cm-1

Absorbance / Wavenumber (cm-1)

File # 1 = PVC3XMG#14 @ 600 6530

pvc3x.mg, an accumulation, 10C/min to 700C

Figure 6. FTIR Spectra of Coal 90003



Hide3D Y-Zoom CURSOR

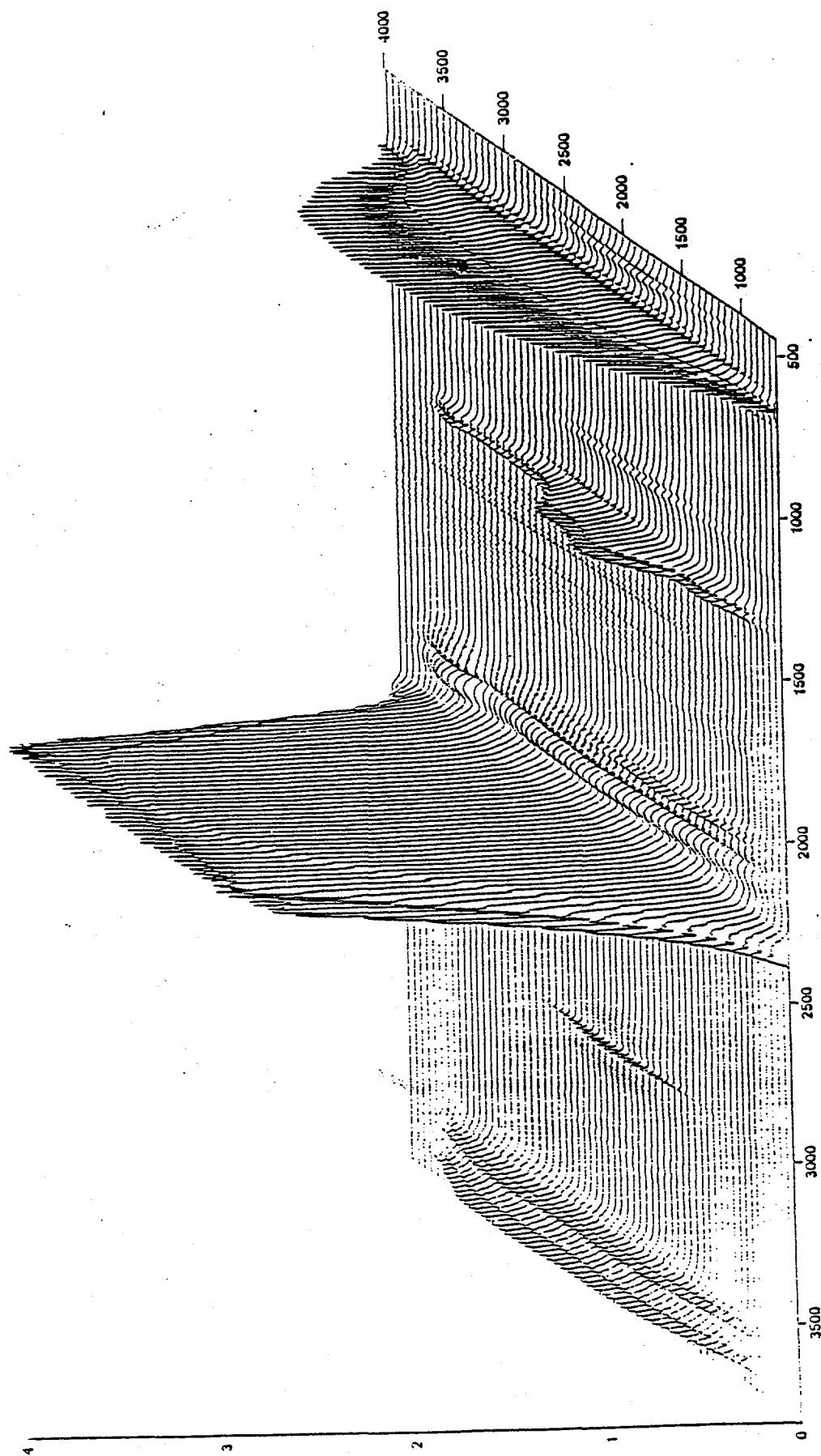
11/27/94 12:59 PM Res=4 cm⁻¹

Absorbance / Wavenumber (cm⁻¹)

File # 1 = C003000#15 @ 766.4512

(XXXX), (XXXX), (XXXX), 100mg, air CO/Min, 10C/min to 700C

Figure 7. FTIR Spectra of Coal 92073



Hide3D Y-Zoom CURSOR

11/4/94 9:26 AM Res=4 cm⁻¹

Absorbance / Wavenumber (cm⁻¹)

File # 1 - C92072#14 @ 600 4735

100/min, Continuum air, 300mg

**Figure 8. Evolved Gas Profiles
for Coal 90003**

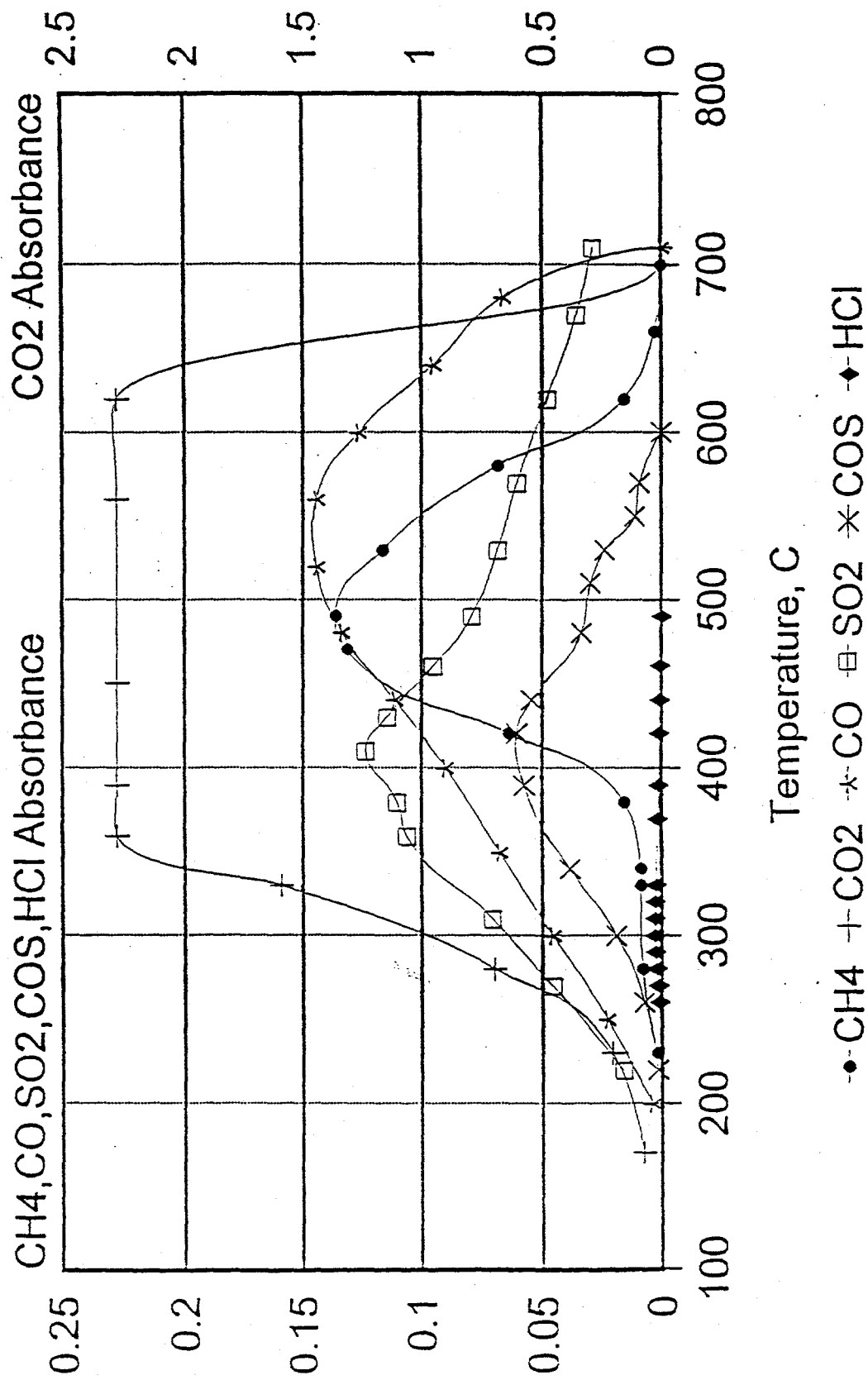


Figure 9. Evolved Gas Profiles for PVC

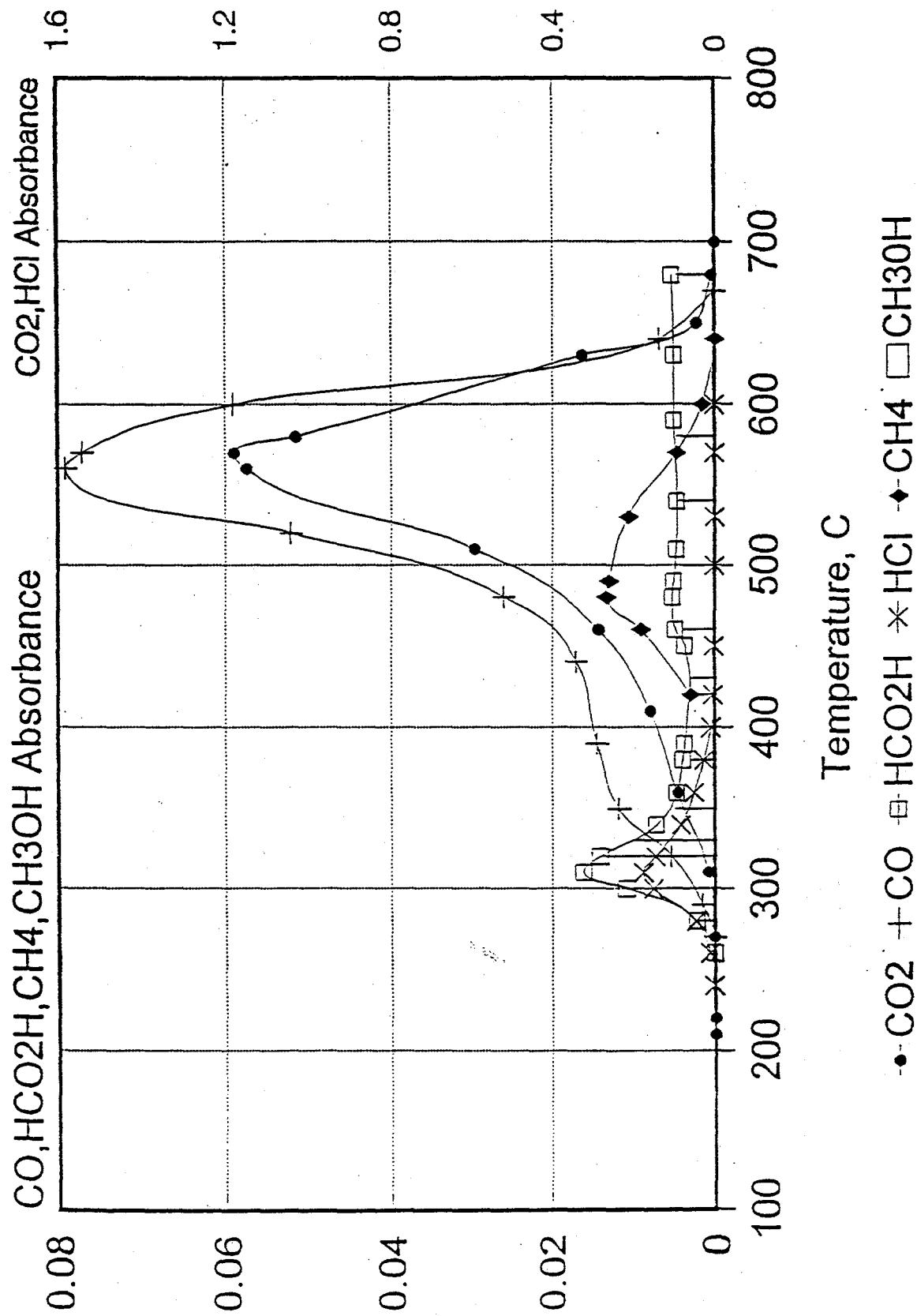
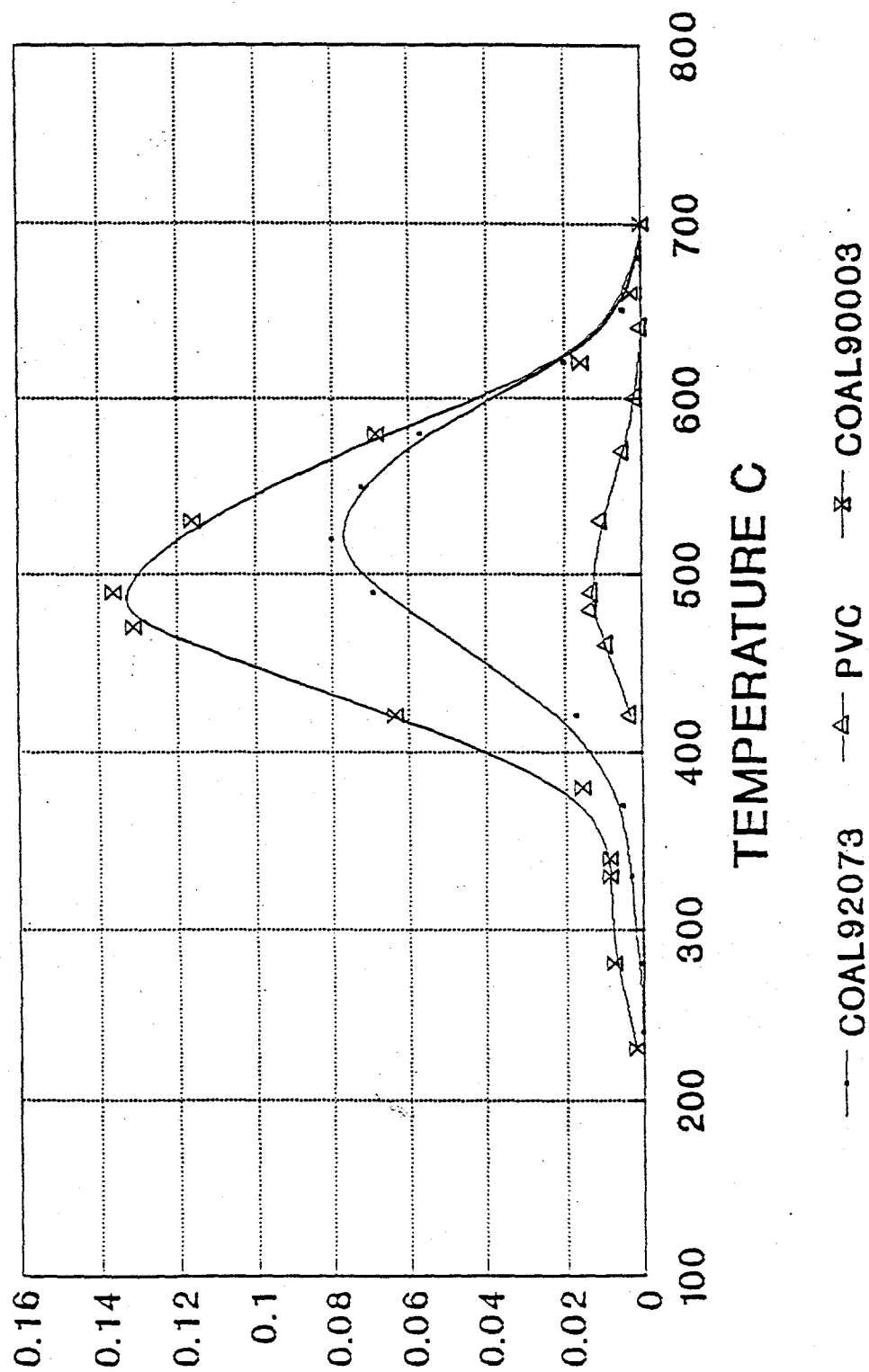
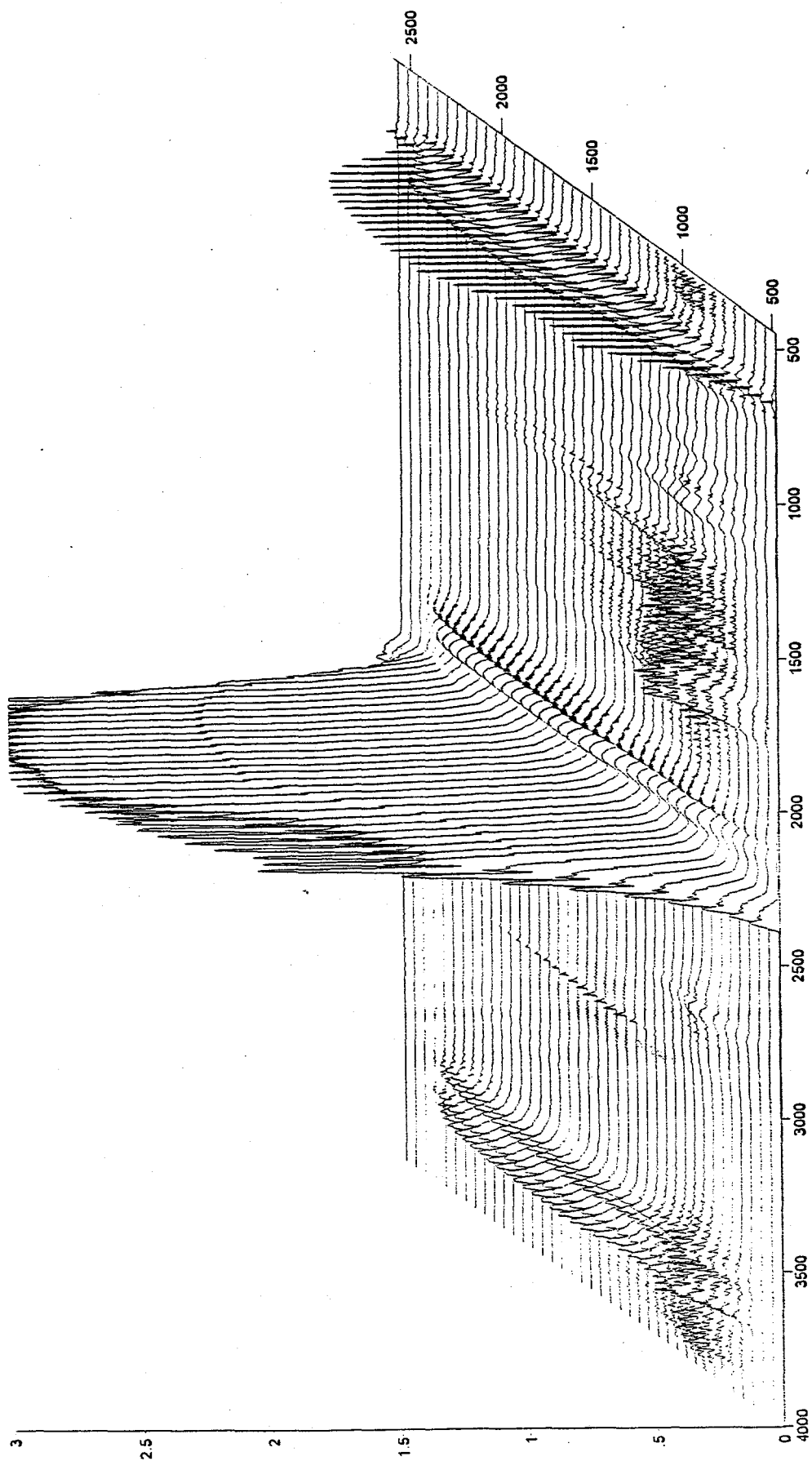


Figure 11. CH₄ Gas Release Profiles





Absorbance / Wavenumber (cm-1)

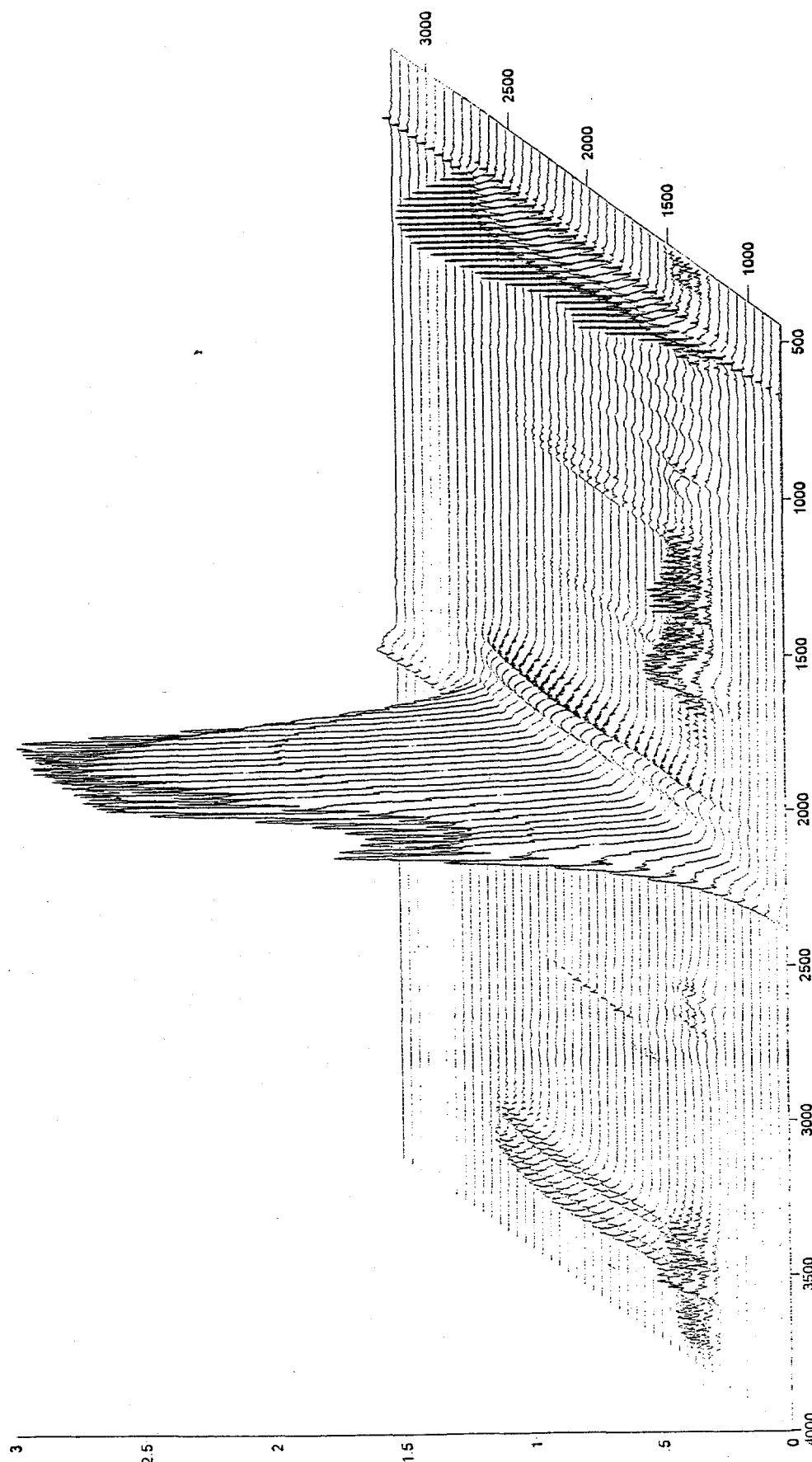
File # 1 = 03NEWS50#10 @ 481.4844

50mg90003 50mgnewspaper in air 50ml/min, 10C/min to 700C

Hide3D Y-Zoom CURSOR

12/25/94 12:55 PM Res=4 cm-1

Figure 12



Absorbance / Wavenumber (cm-1)

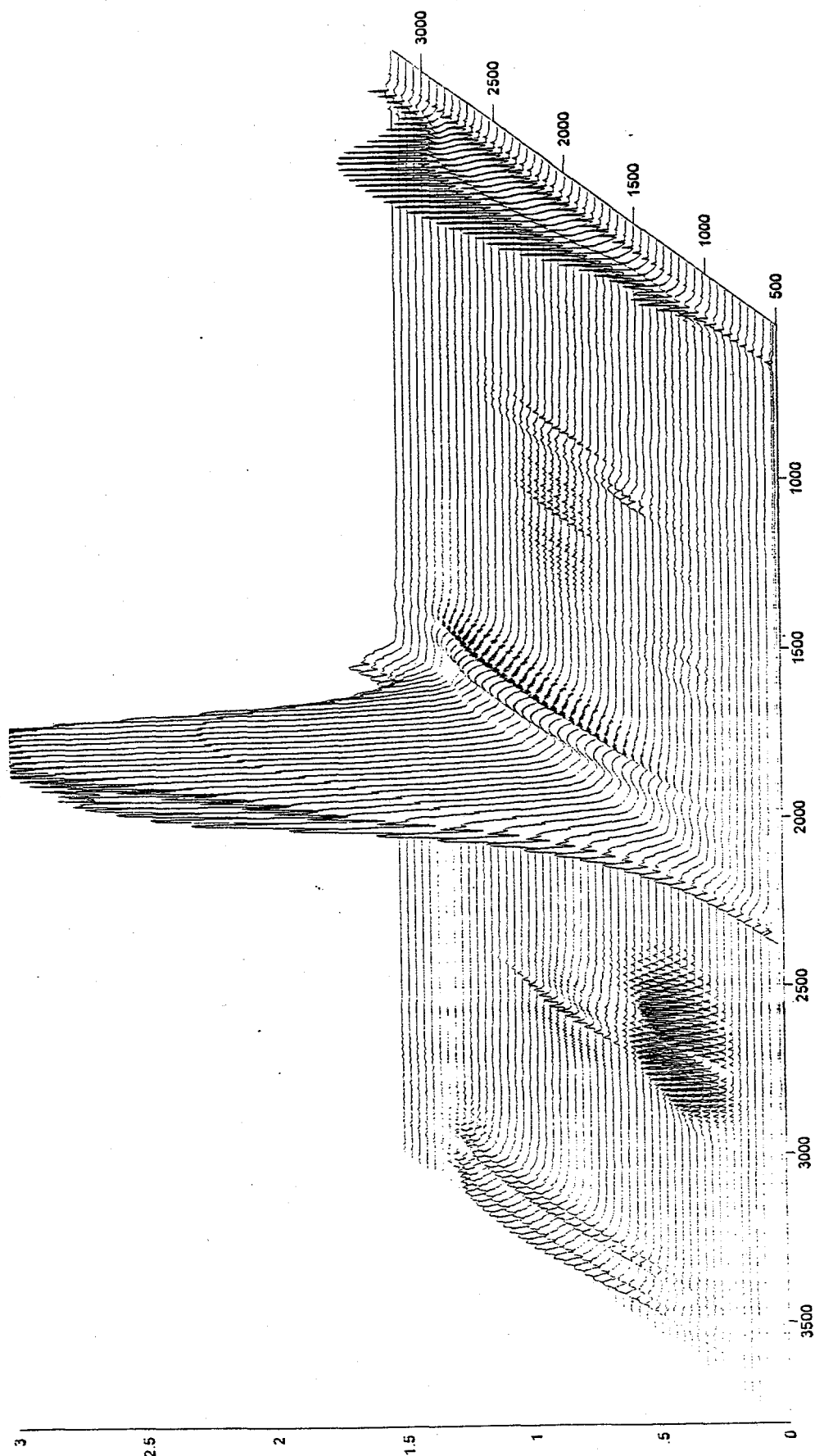
File # 1 = 03CELL50#16 @ 802.3779

50mg/500003.50mgcellulose in air 50ml/min, 10C/min to 700C

Hide3D Y-Zoom CURSOR

12/24/94 11:27 AM Res=4 cm-1

Figure 13



Absorbance / Wavenumber (cm-1)

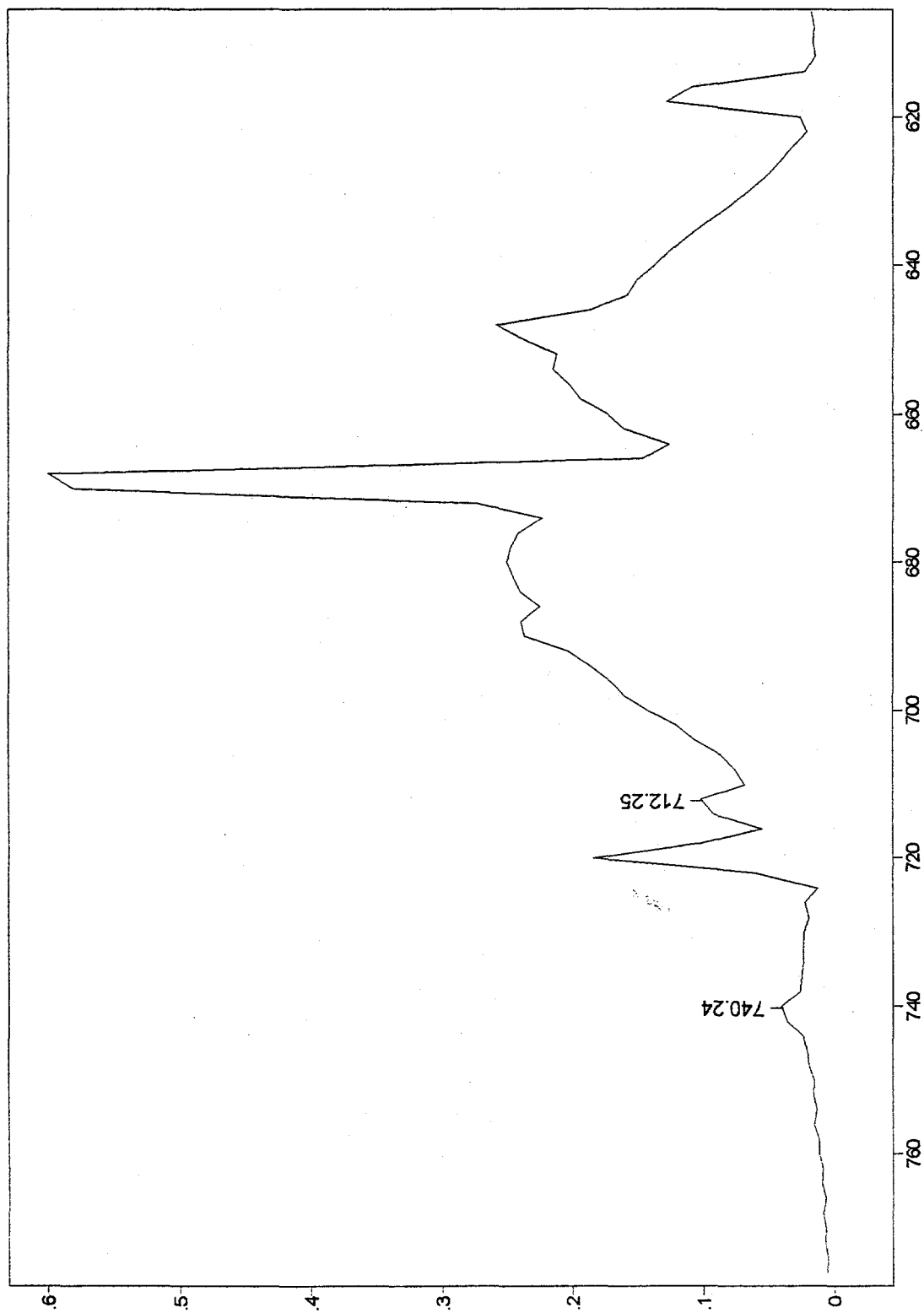
File # 1 = 03PVC50#14 @ 696.144

90003-50mg.pvc50mg in air 50ml/min, 10c/min to 700c

Hlde3D Y-Zoom CURSOR

12/23/94 2:56 PM Res=4 cm-1

Figure 14



Absorbance / Wavenumber (cm-1)

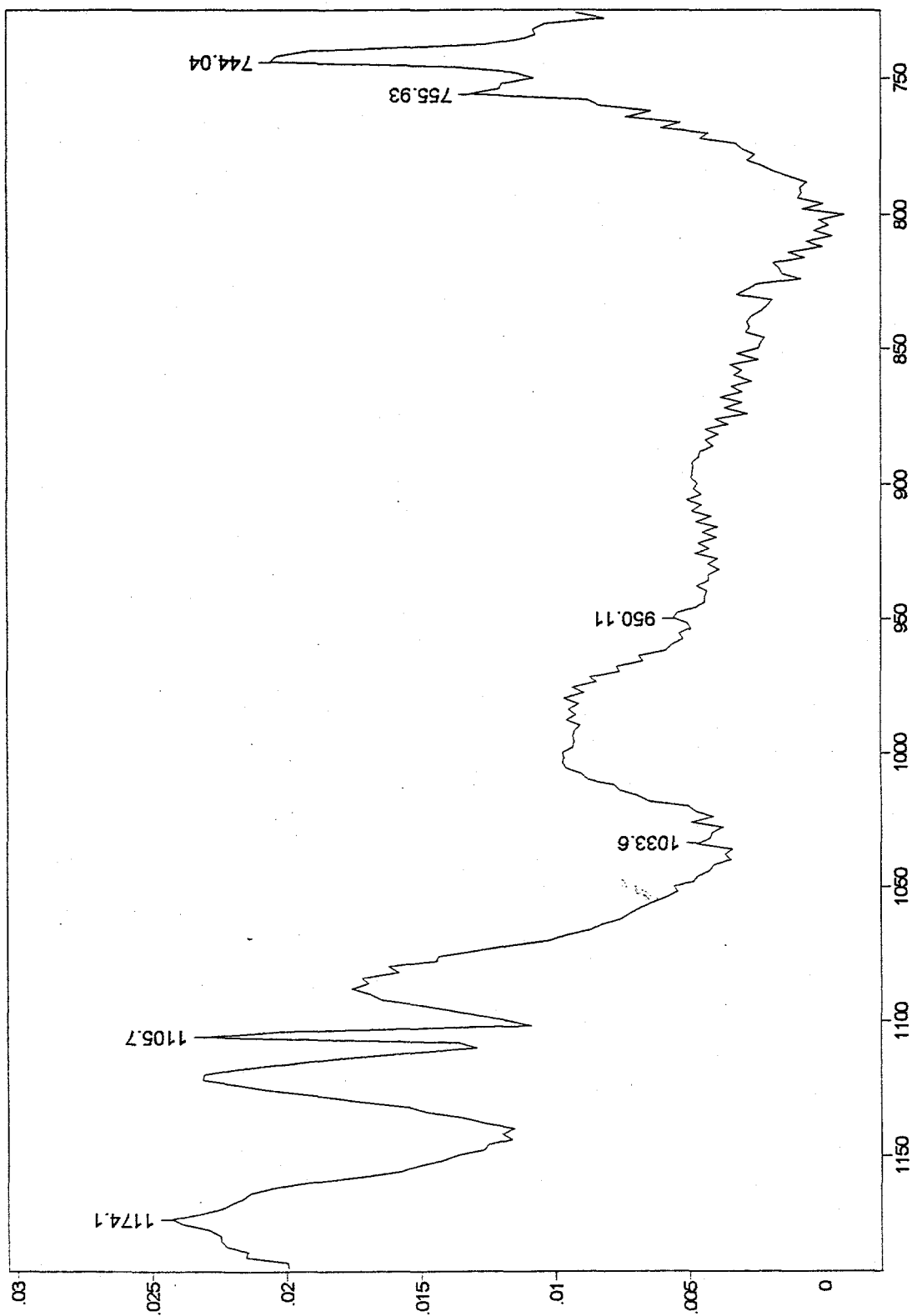
File # 1 = 035122#40 @ 2067.511

50mg90003, 10mgpvc, 20mgcellulose, 20mgnewsaper in air 50ml/min, 10C/min to 700C

Paged Y-Zoom CURSOR

1/7/95 2:34 PM Res=4 cm-1

Figure 15



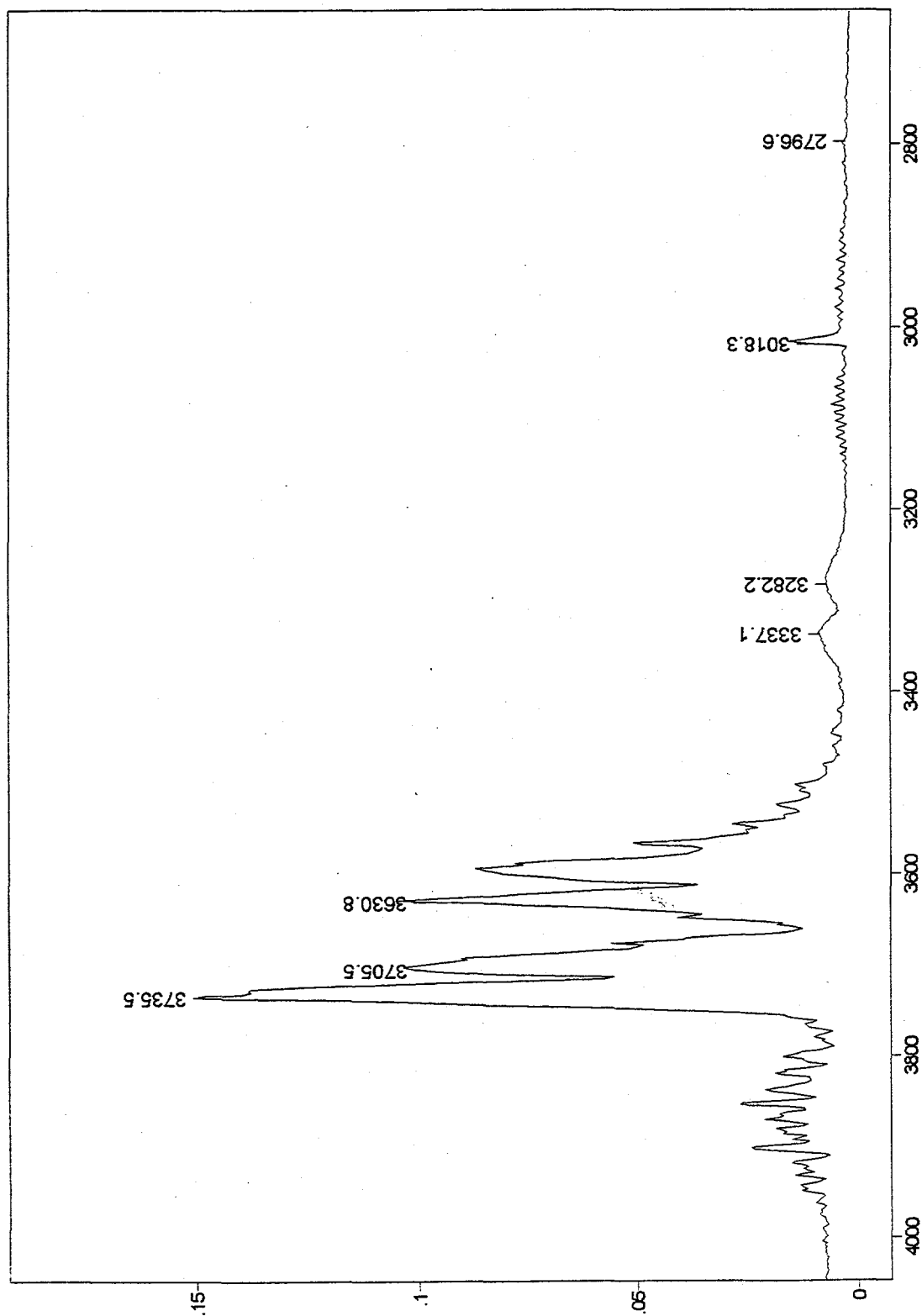
Paged Y-Zoom CURSOR

File # 1 = 035122#22 @ 1113.275

50mg90003, 10mgpvc, 20mgcellulose, 20mgnewspaper in air 50ml/min, 10C/min to 700C

1/7/95 2:34 PM Res=4 cm-1

Figure 16



Absorbance / Wavenumber (cm-1)

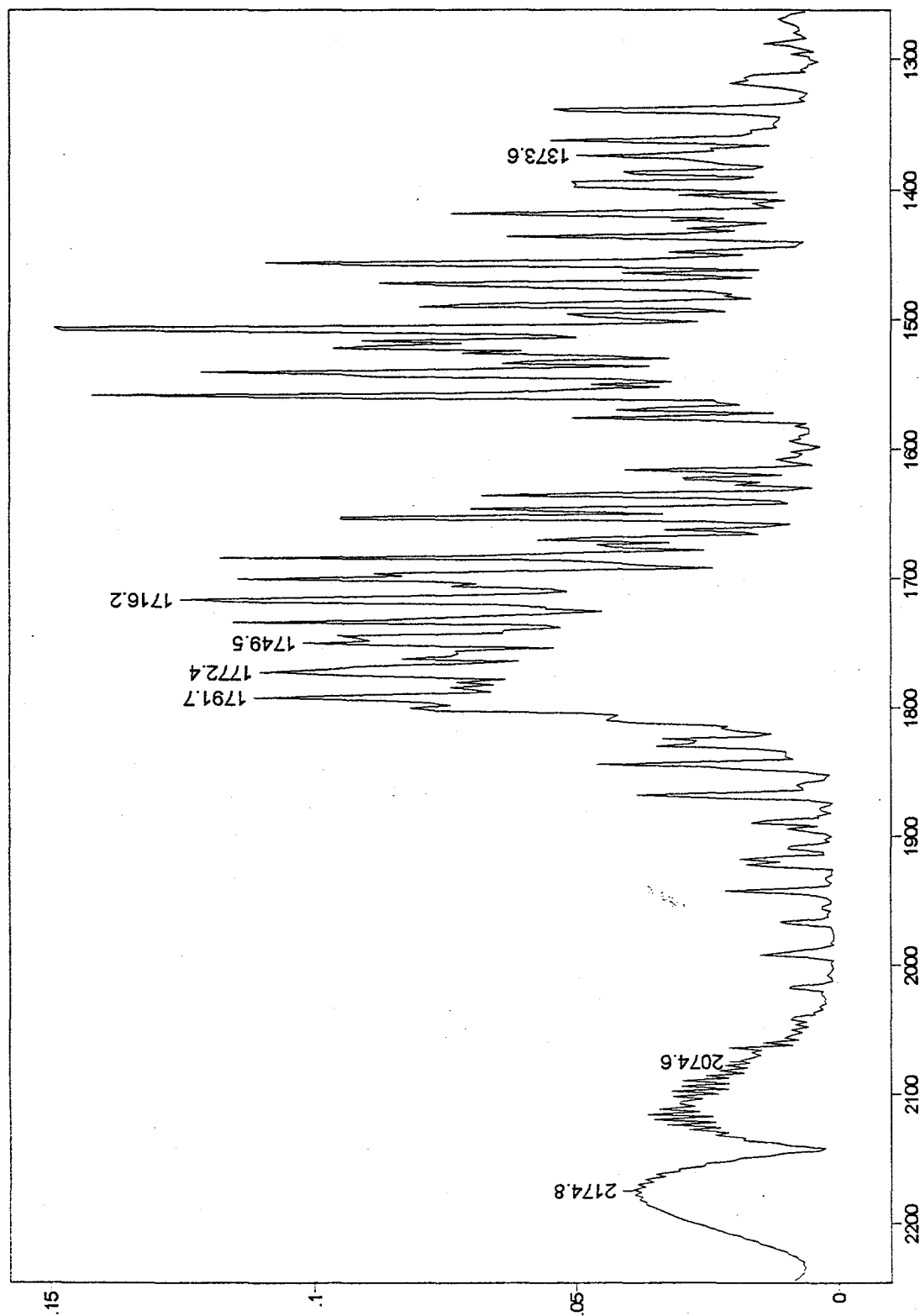
File # 1 = 035122#40 @ 2067.511

50mg90003, 10mgpvc, 20mgcellulose, 20mgnewspaper in air 50ml/min, 10C/min to 700C

Paged Y-Zoom CURSOR

17/95 2:34 PM Res=4 cm-1

Figure 17



Absorbance / Wavenumber (cm-1)

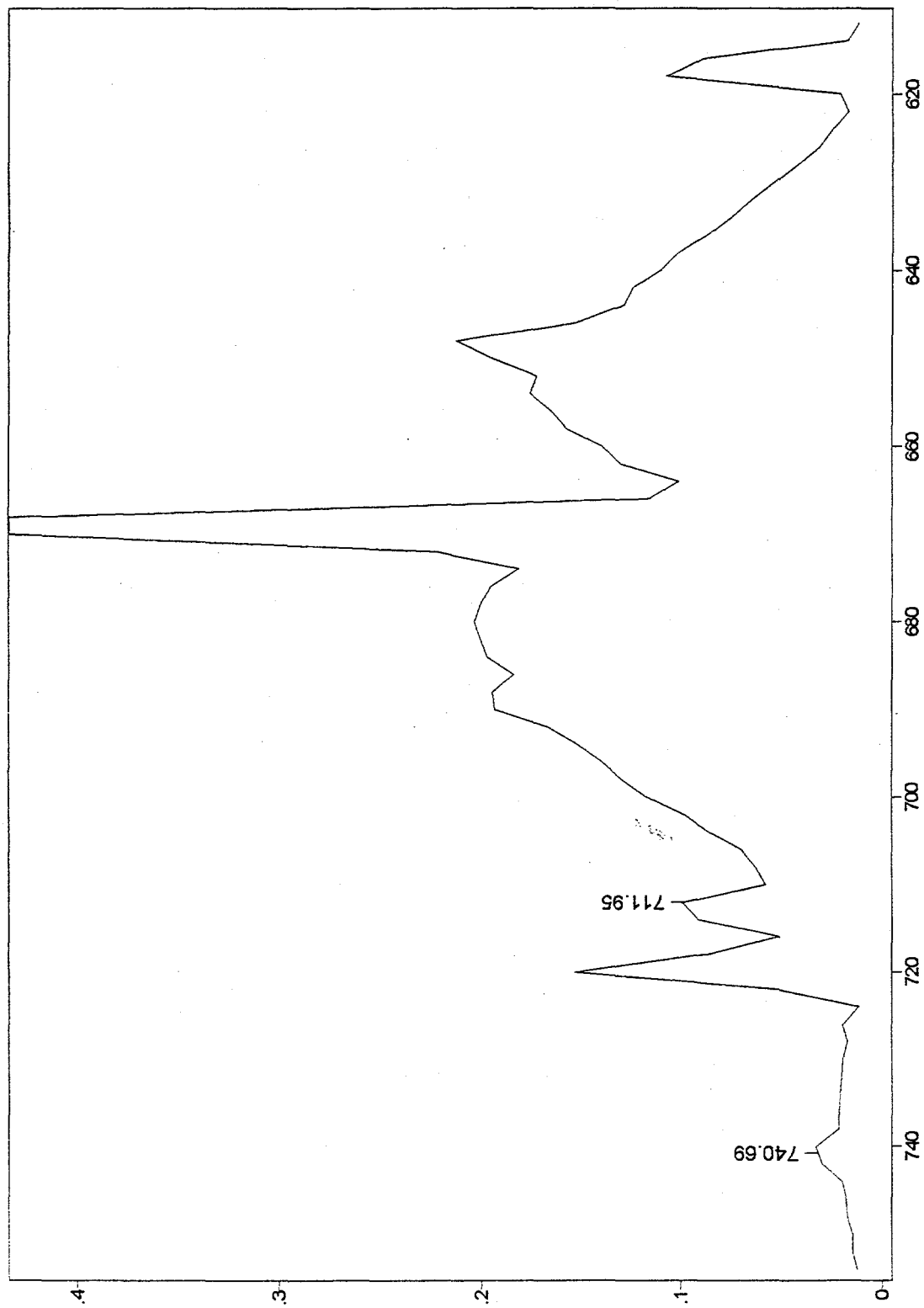
File # 1 = 035122#20 @ 1007.249

50mg90003, 10mgpvc, 20mgcellulose, 20mgnews paper in air 50ml/min, 10C/min to 700C

Paged Y-Zoom CURSOR

1/7/95 2:34 PM Res=4 cm-1

Figure 18



Absorbance / Wavenumber (cm-1)

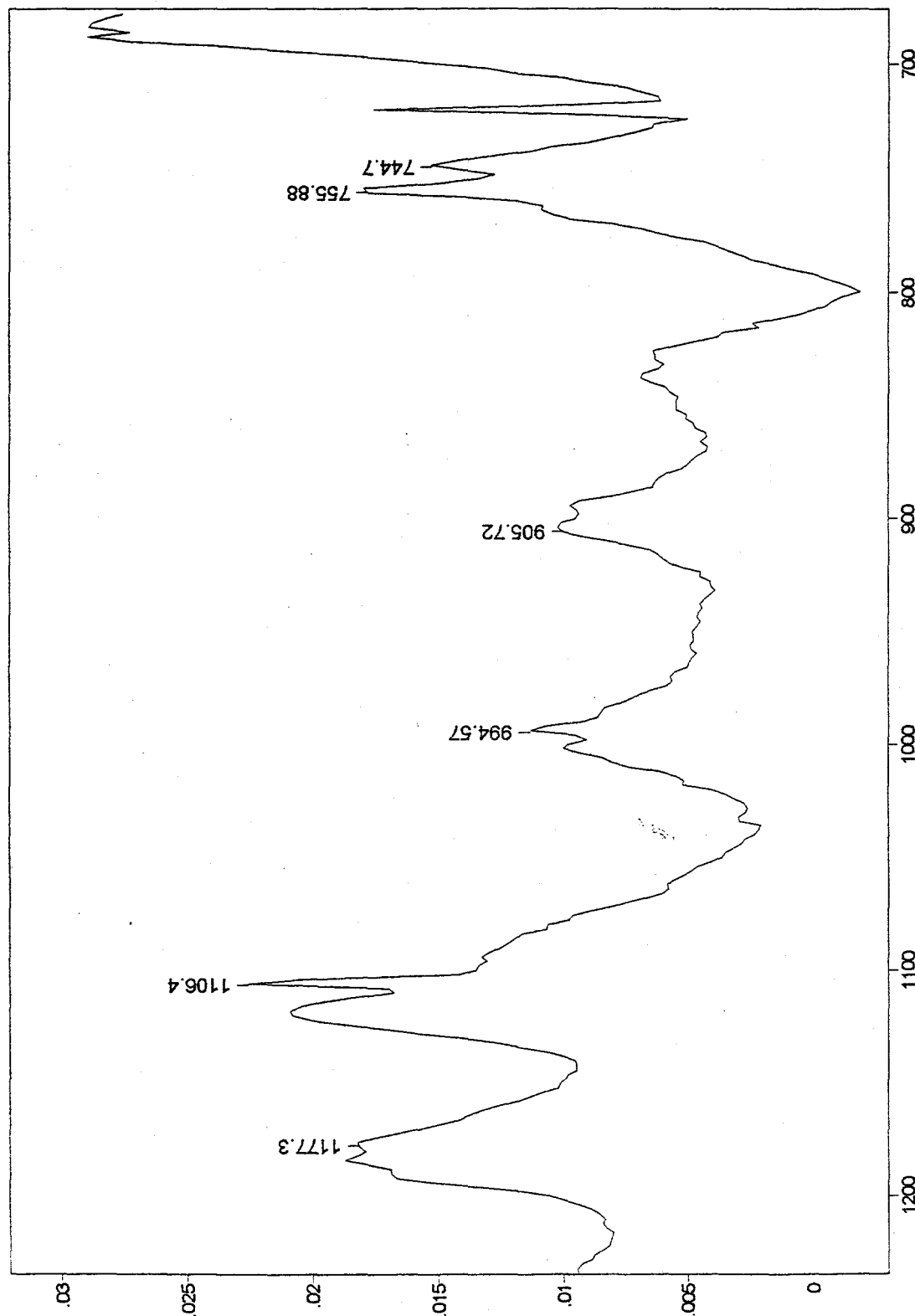
File # 1 = 735122#43 @ 2247.889

92073-50mg,pvc10mg,news20mg,cellulose10mg in air 50ml/min, 10c/min to 700c

Paged Y-Zoom CURSOR

12/23/94 1:29 PM Res=4 cm-1

Figure 19



Absorbance / Wavenumber (cm-1)

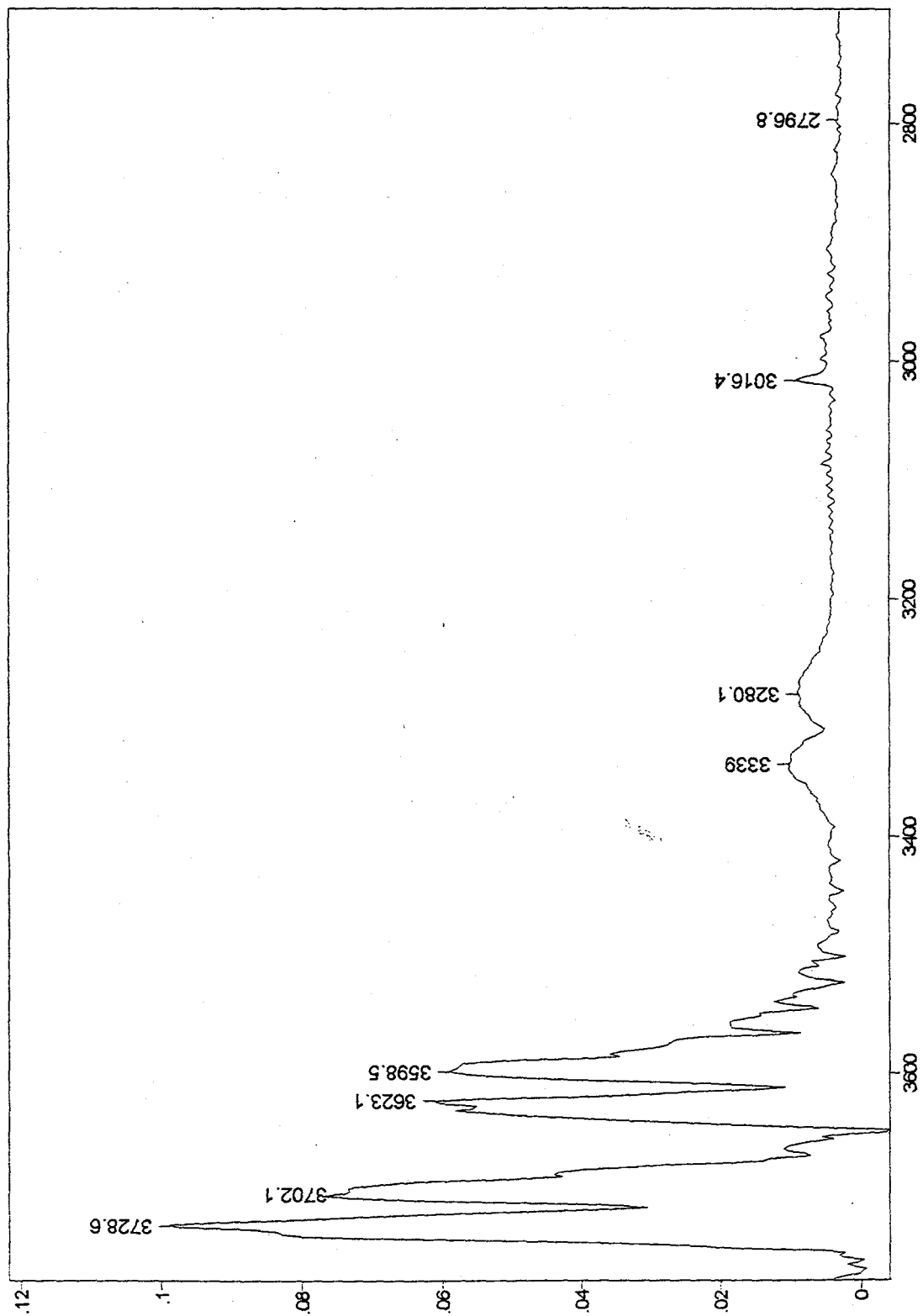
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92073-50mg,pvc10mg,news20mg,cellulose10mg in air 50ml/min,10c/min to 700c

Paged Y-Zoom CURSOR

12/23/94 1:29 PM Res=4 cm-1

Figure 20



Absorbance / Wavenumber (cm-1)

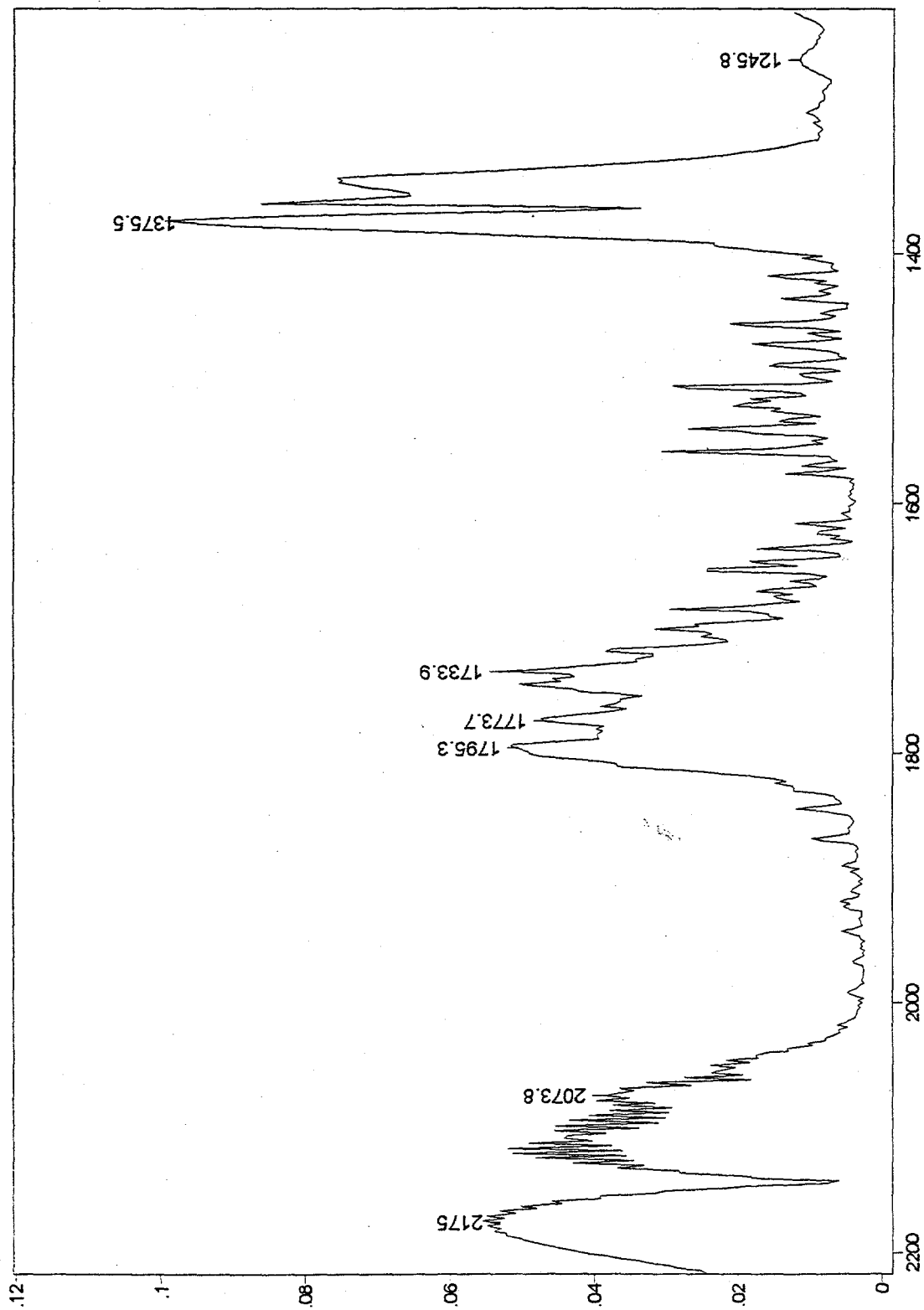
File # 1 = 735122#43 @ 2247.889

92073-50mg,pvc10mg,news20mg,cellulose10mg in air 50ml/min,10c/min to 700c

Paged Y-Zoom CURSOR

12/23/94 1:29 PM Res=4 cm-1

Figure 21



Absorbance / Wavenumber (cm-1)

File # 1 = 735122#28 @ 1445.071

92073-50mg,pvc10mg,news20mg,cellulose10mg in air 50ml/min,10c/min to 700c

Paged Y-Zoom CURSOR

12/23/94 1:29 PM Res=4 cm-1

Figure 22

Figure 23

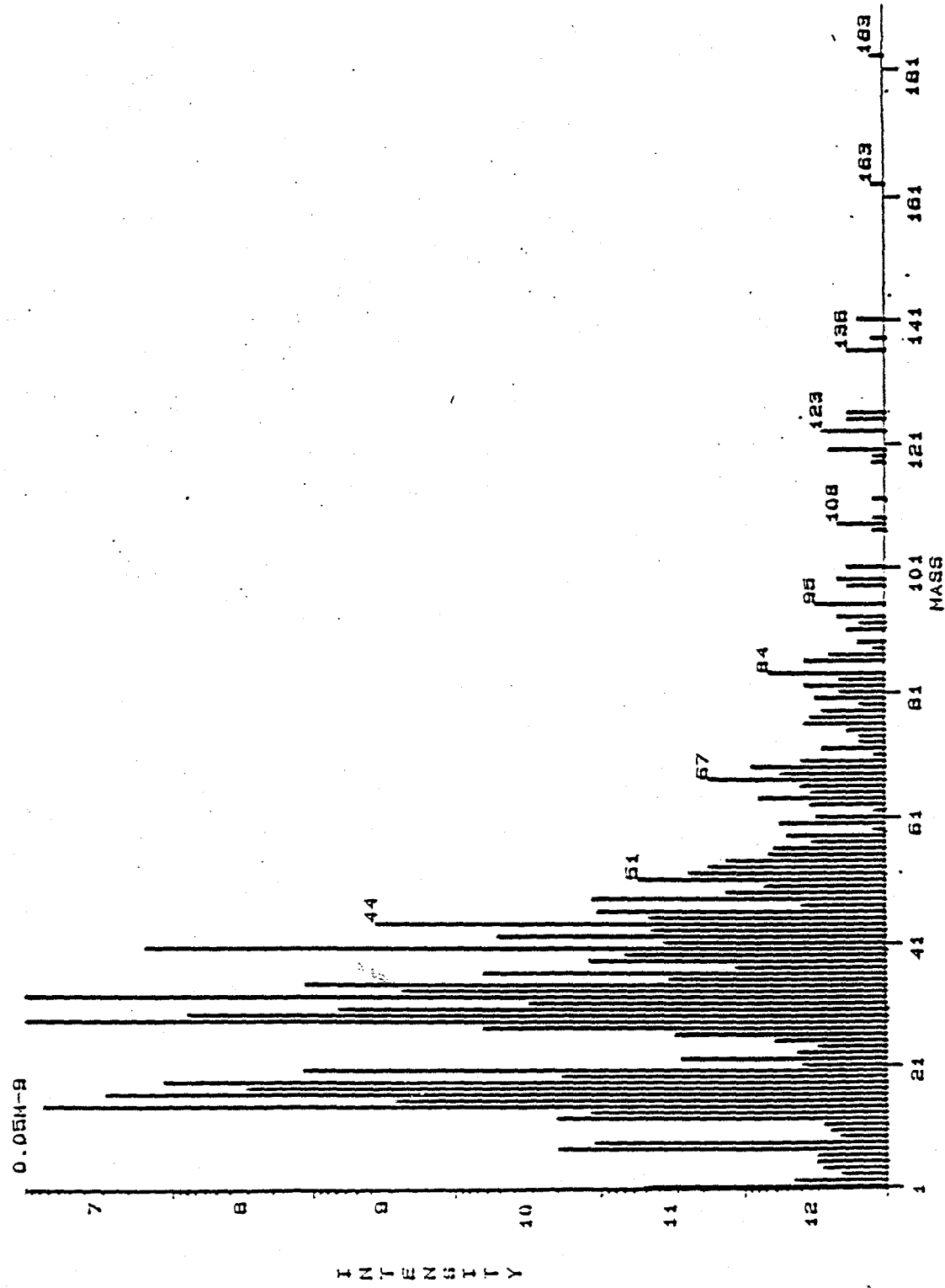
Mass-to-Charge Ratios for Scan 26 in TG-MS Analysis of Coal 92073

Time: 00:07:10

Scan: 26

File: C82073

05:06 14-Apr-85



A1: 0.07 A2:

Cursor - 1

Created: 19:36:21

29-Dec-84

Figure 24 Evolved Gas Profiles for Coal 92073

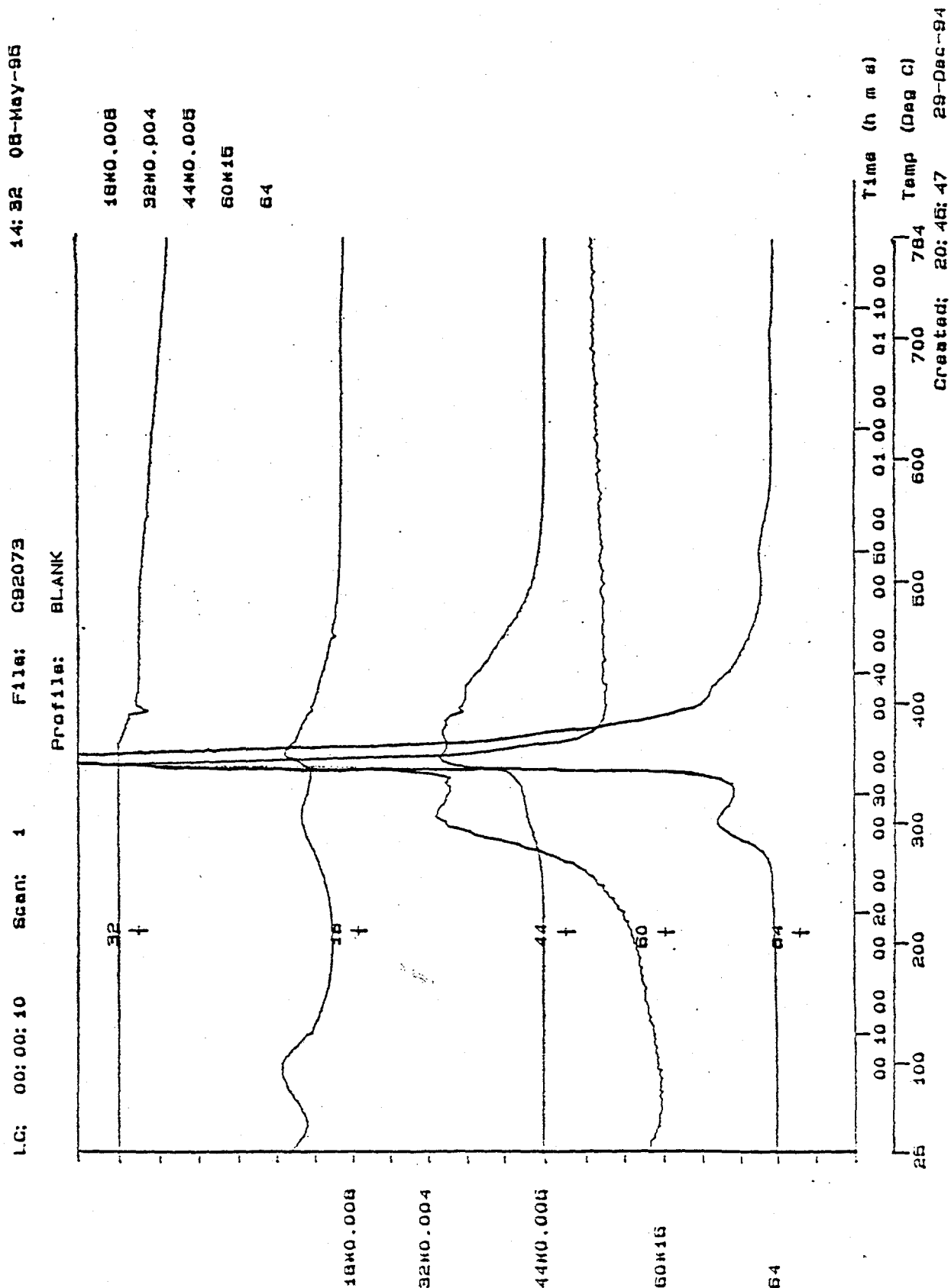


Figure 25 Evolved Gas Profiles for Combustion Gases for PVC

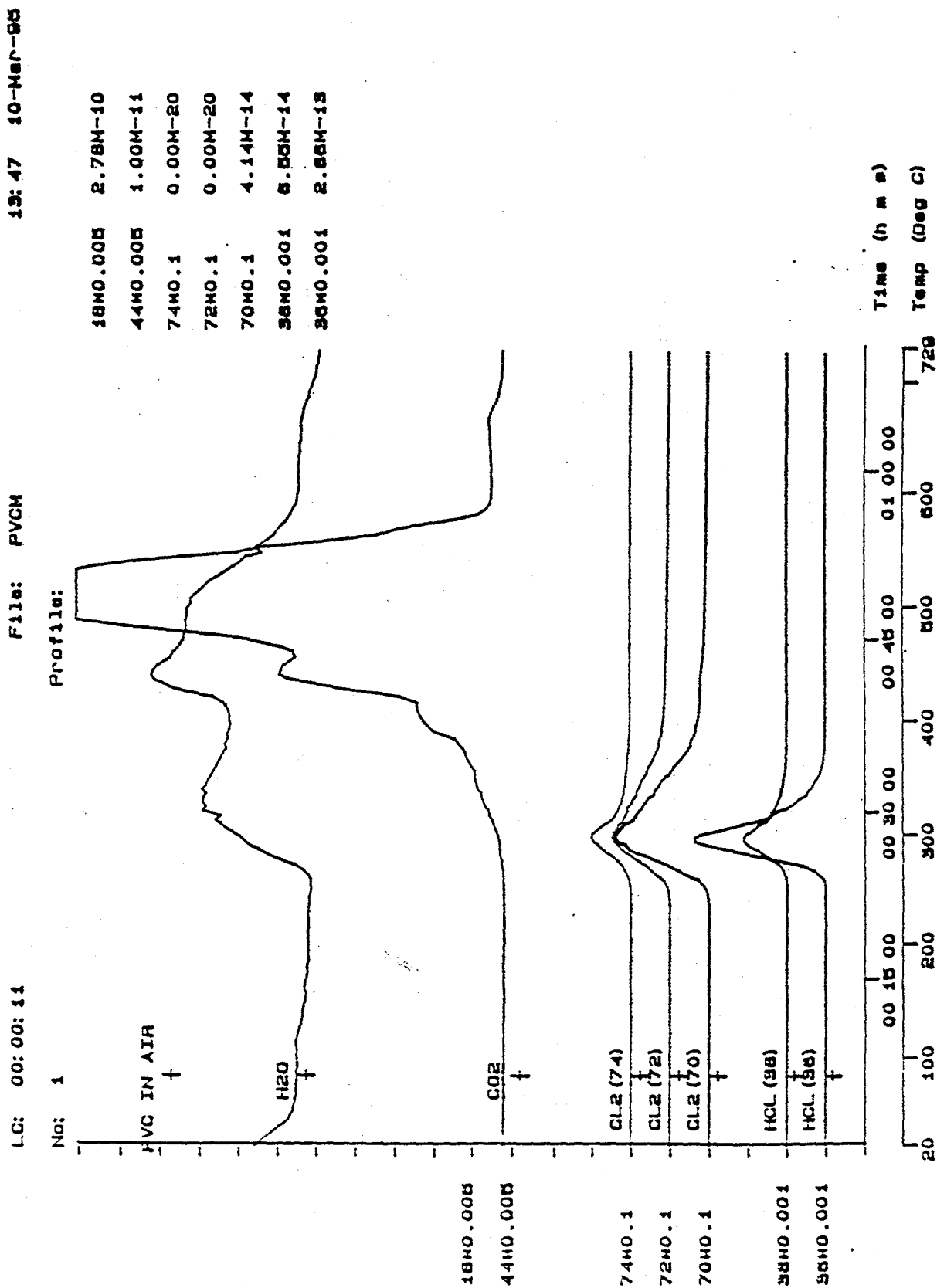


Figure 26 Profiles for HCl and Cl₂ Evolved During Combustion of PVC

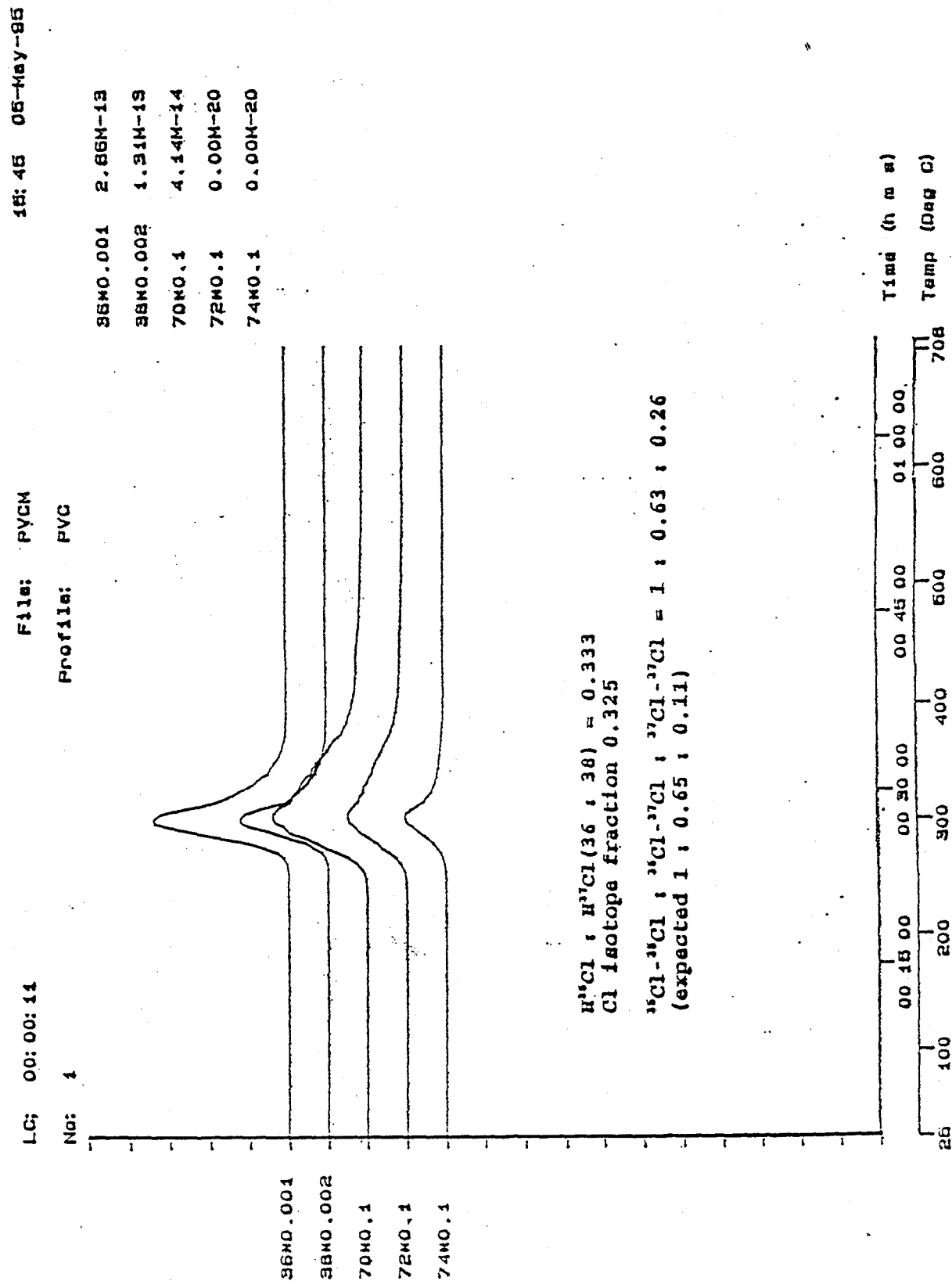
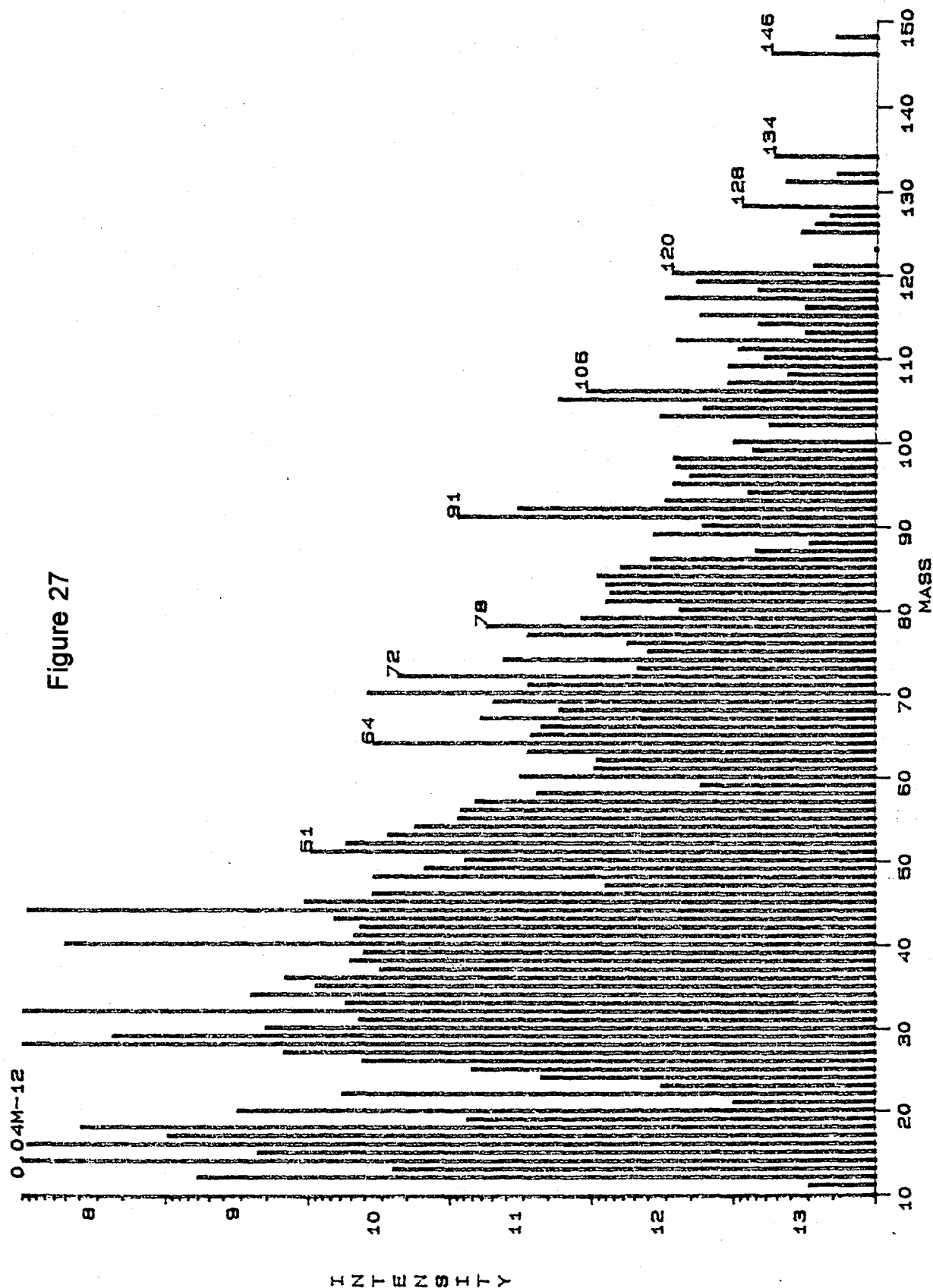


Figure 27

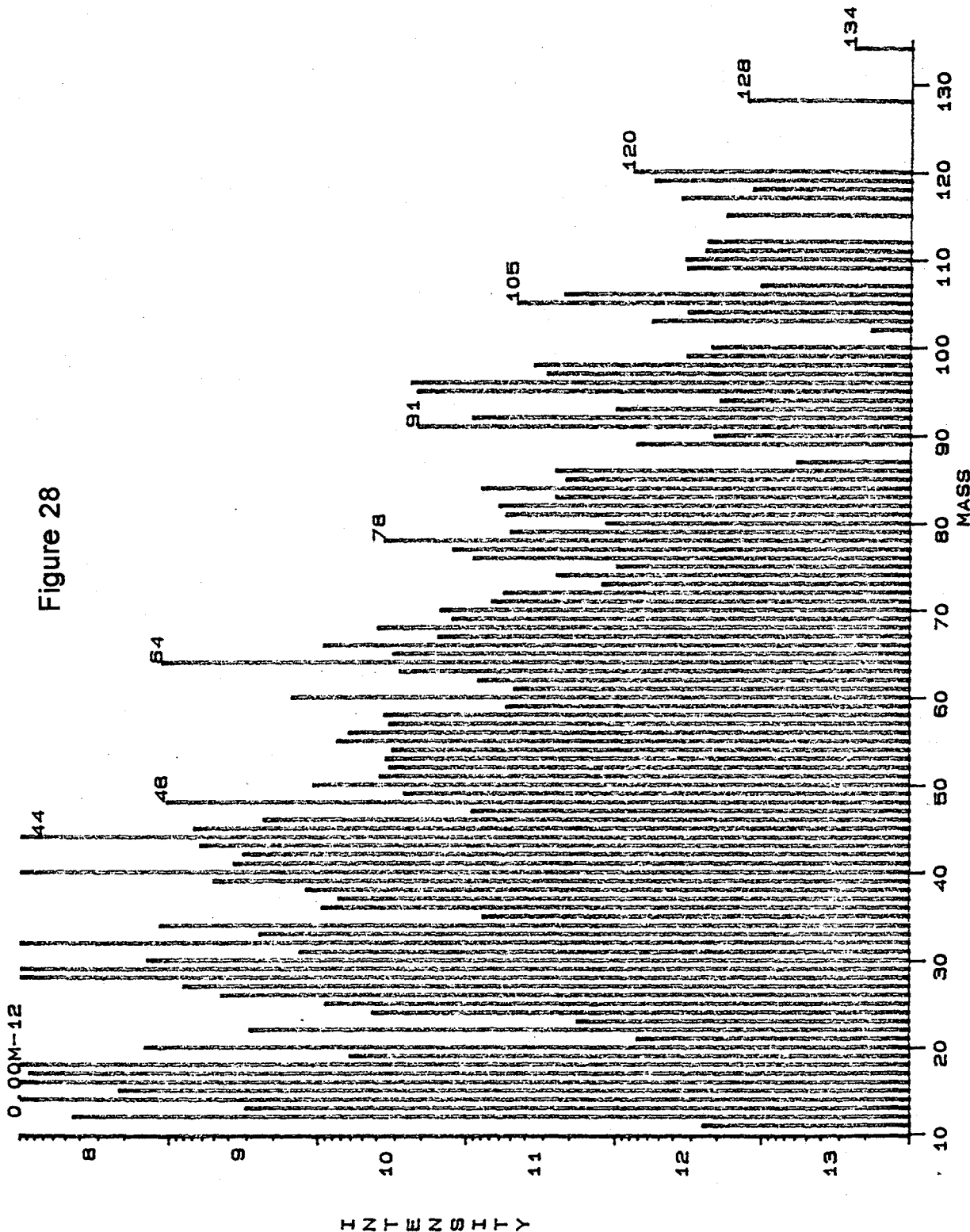


22: 18 26-May-95

File: 73NEW50

Scan: 75

Time: 00: 29: 28

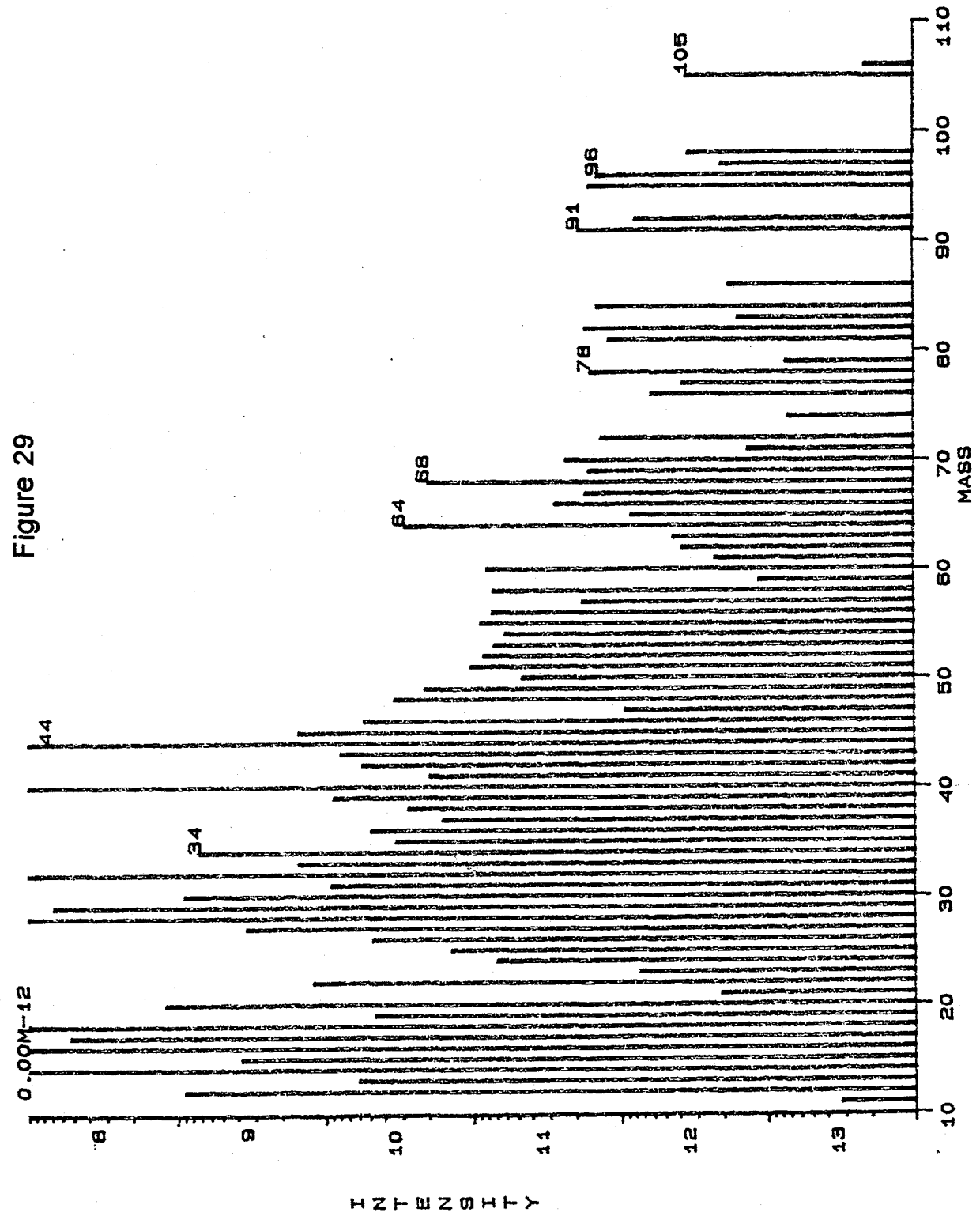


A1: -0.02 A2:

Cursor = 10

Created: 14: 06: 05

12-Jan-95

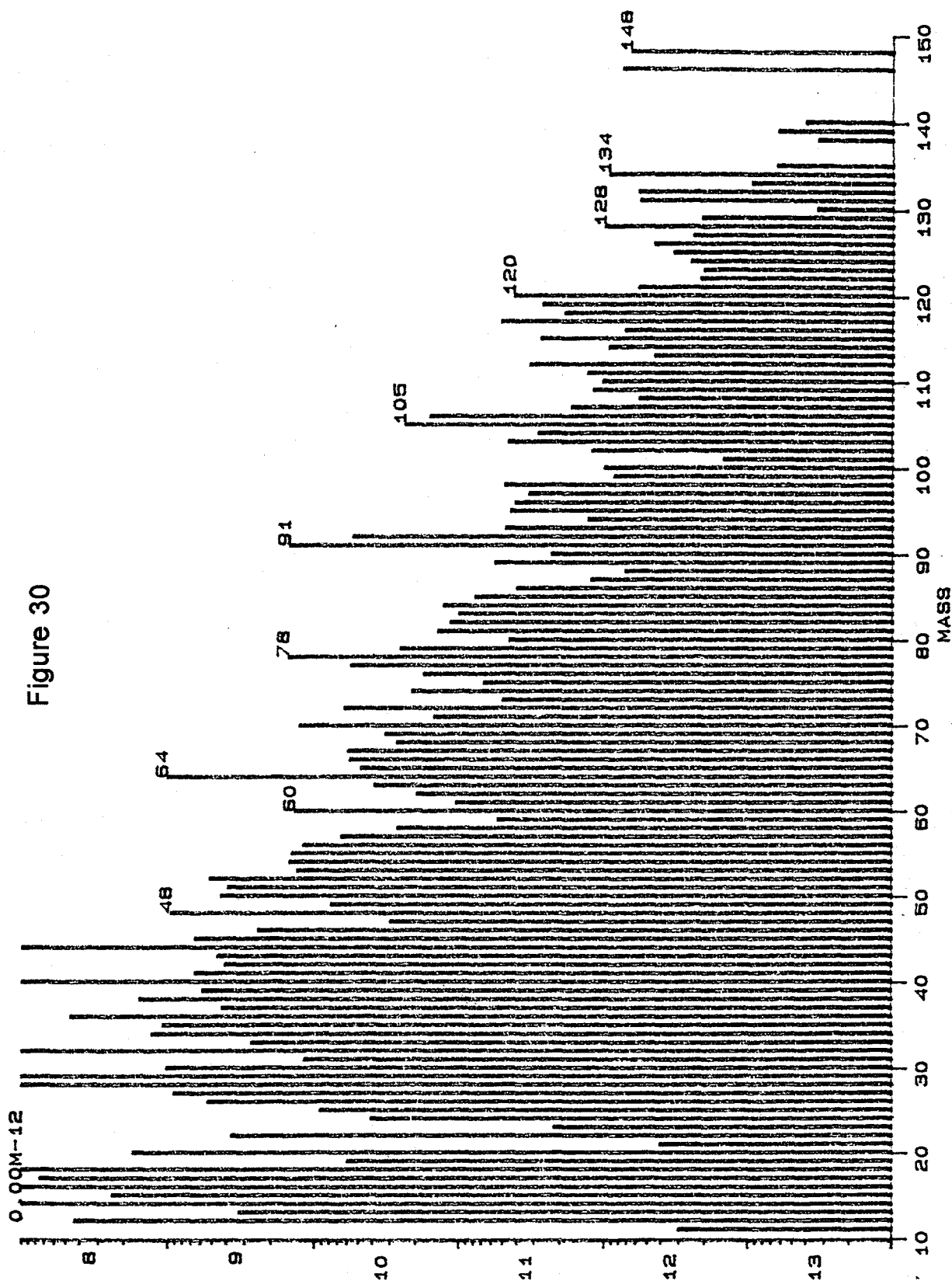


22:24 26-May-95

File: 73P25N25

Scan: 77

Time: 00:30:54



A1: -0.02 A2:

Cursor = 10

Created: 18:28:44

12-Jan-95

22:08 26-May-95

File: 735122

Scan: 76

Time: 00:30:17

3.94M-9

Figure 31

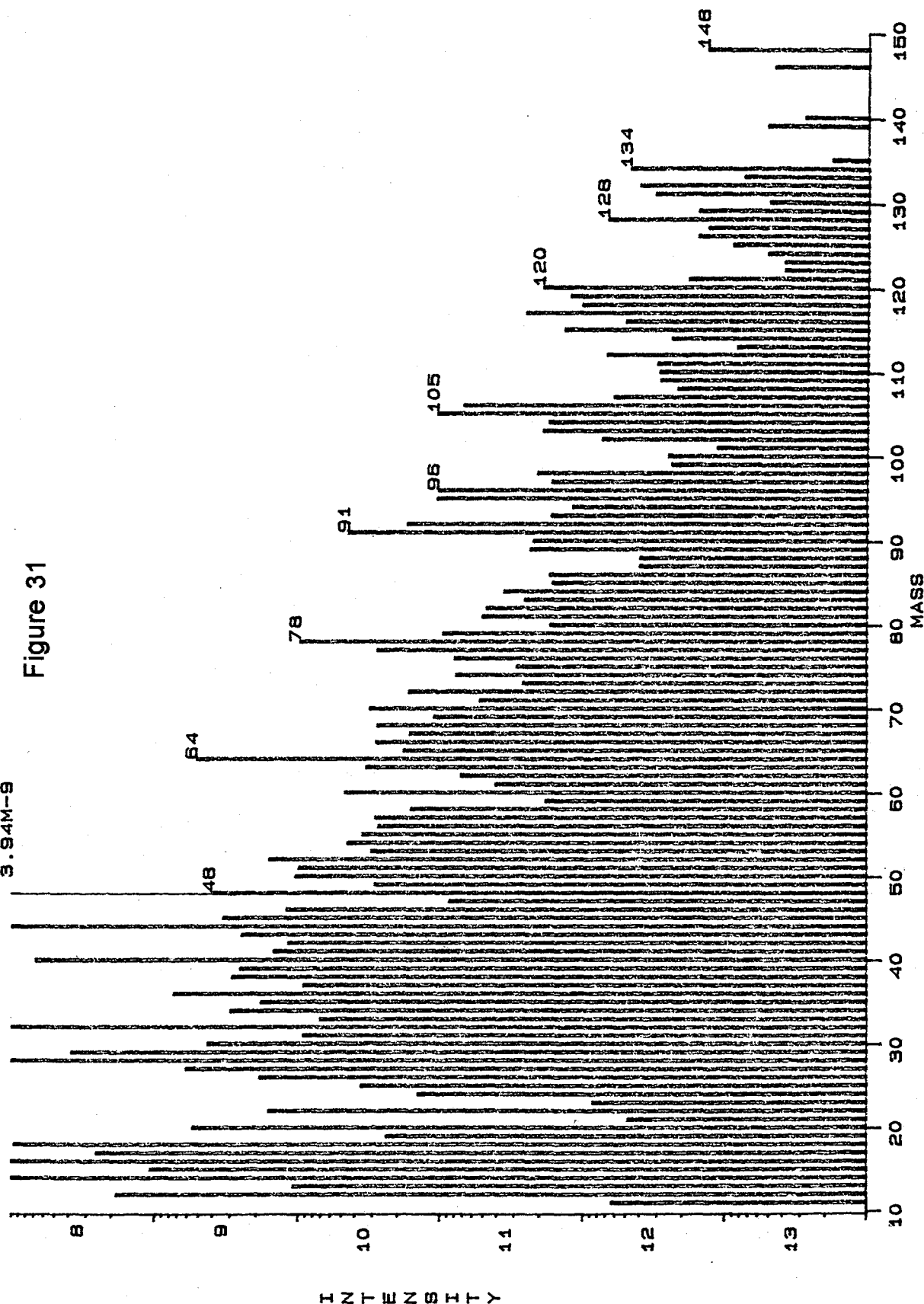
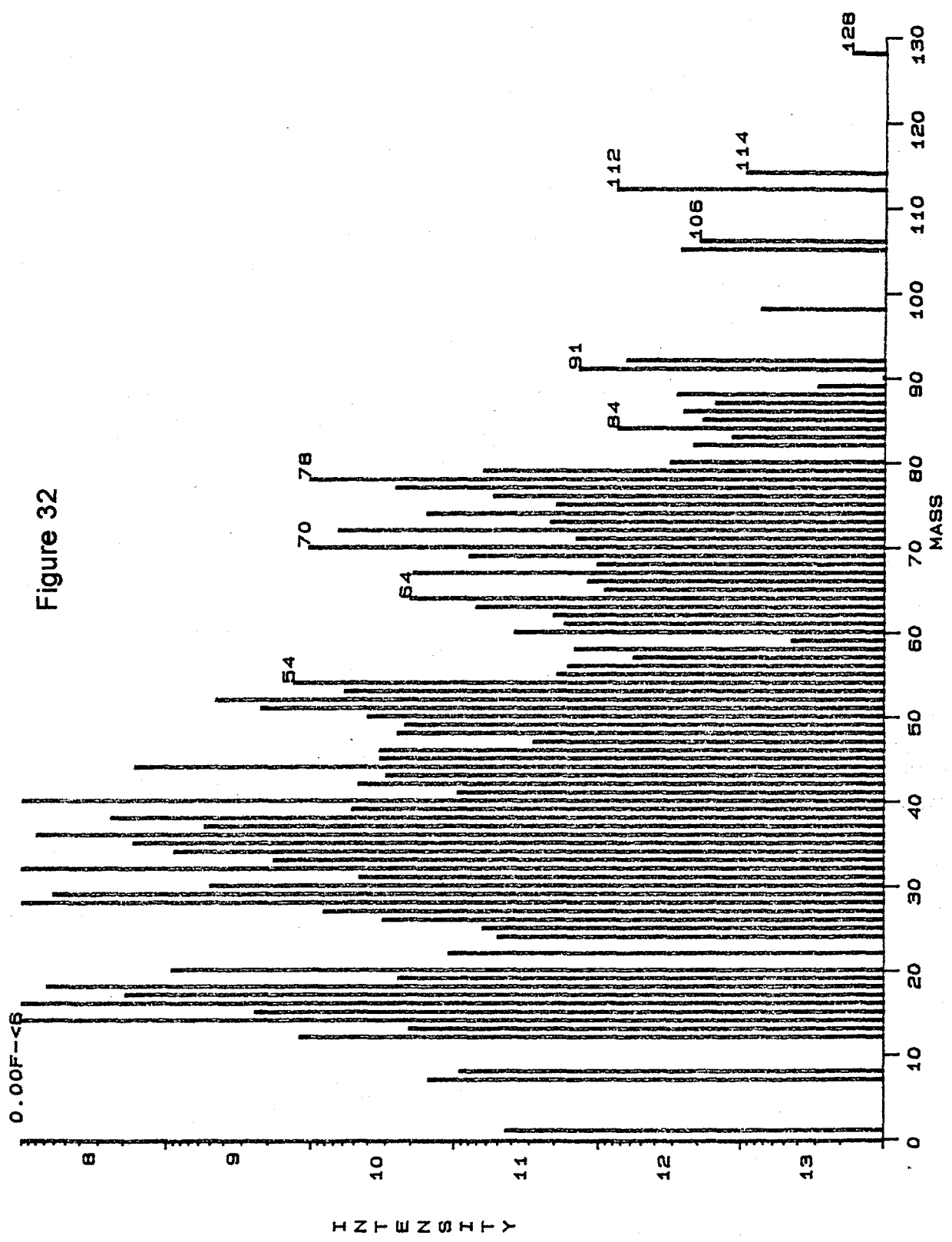
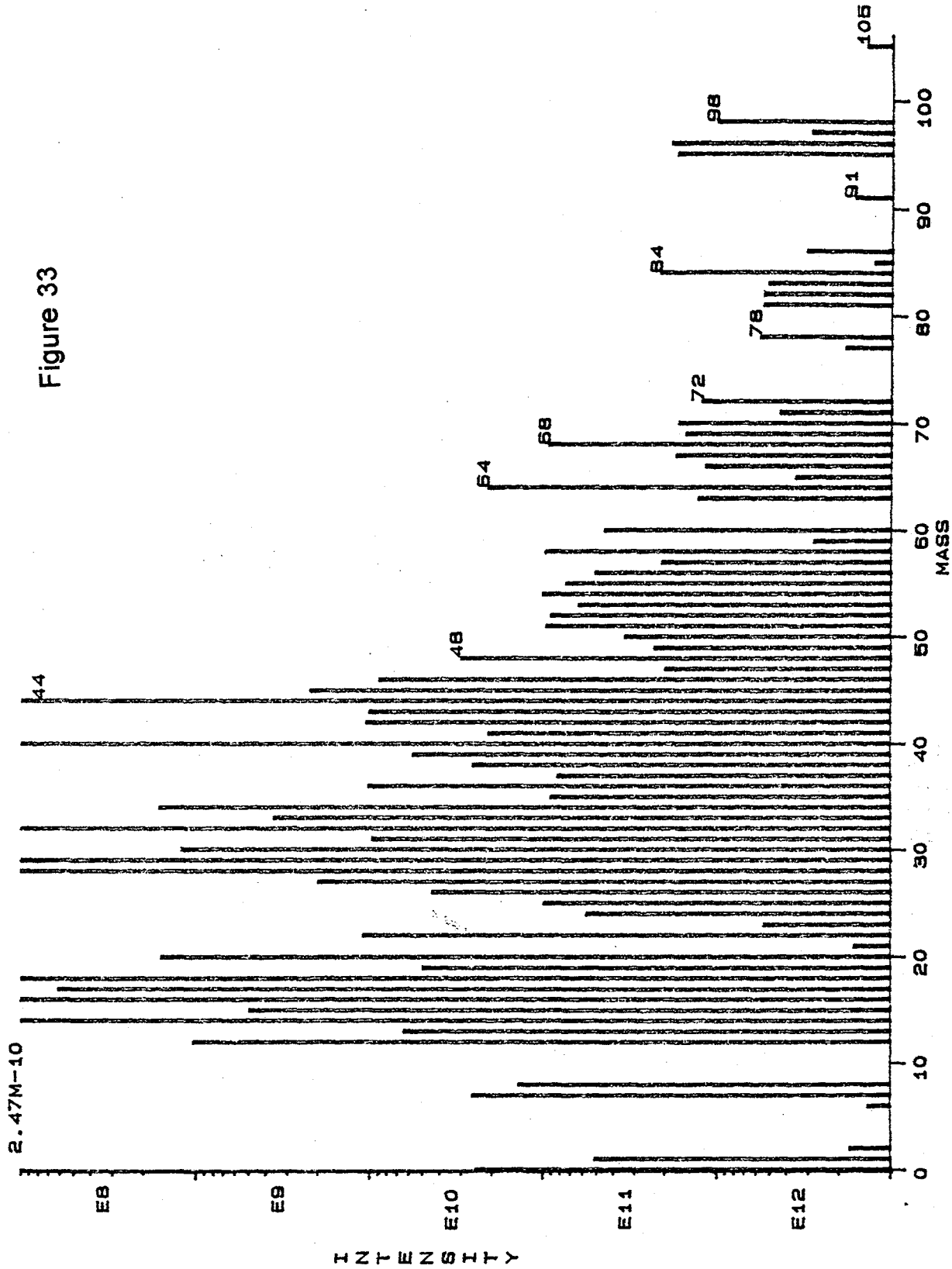


Figure 32



Time: 00:30:50 Scan: 78 File: 03CEL50 21:50 26-May-95

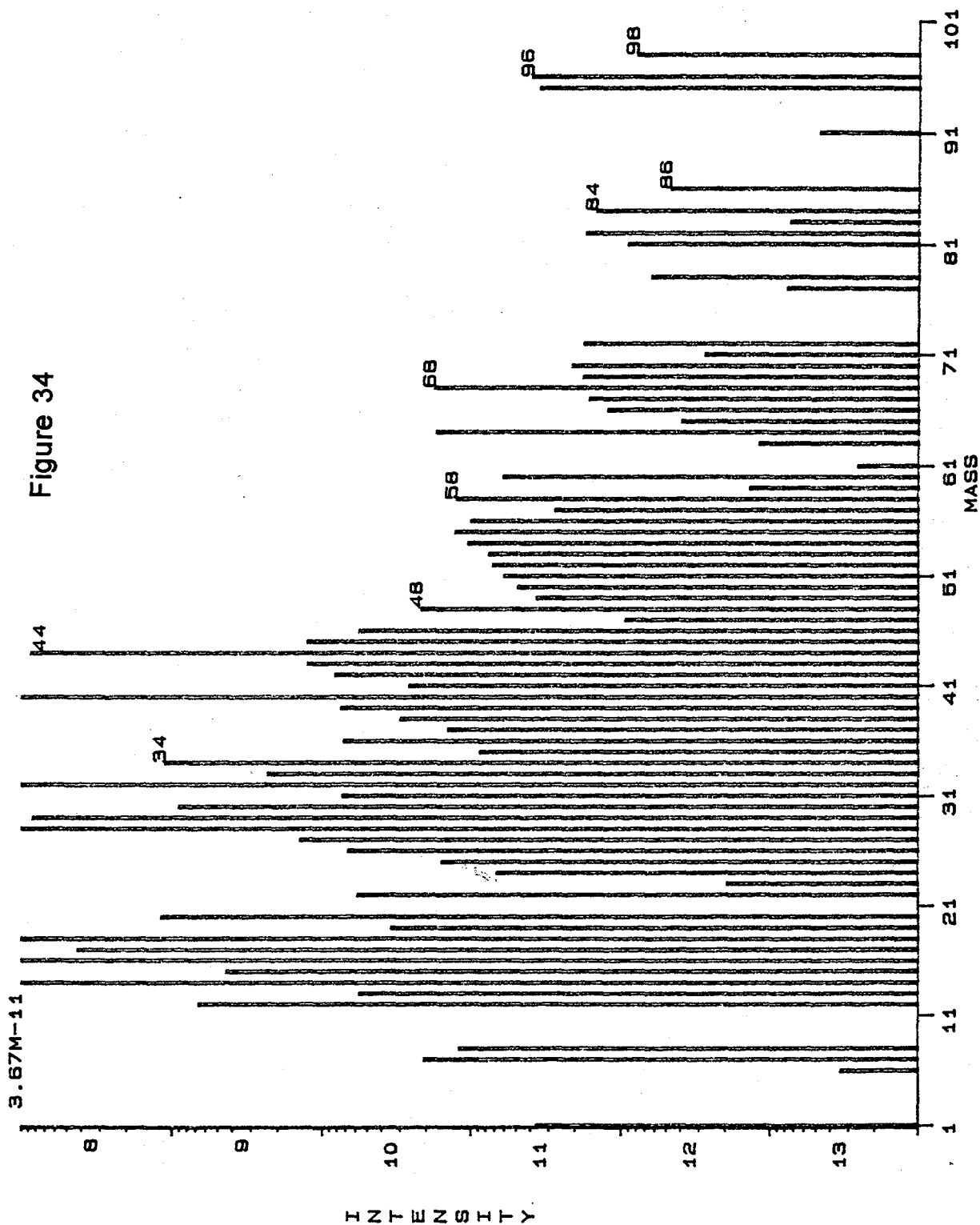


Time: 00:30:46

File: 03NEW50

Scan: 78

21:39 26-May-95



A1: 0.00 A2:

Cursor = 1

Created: 19:23:06

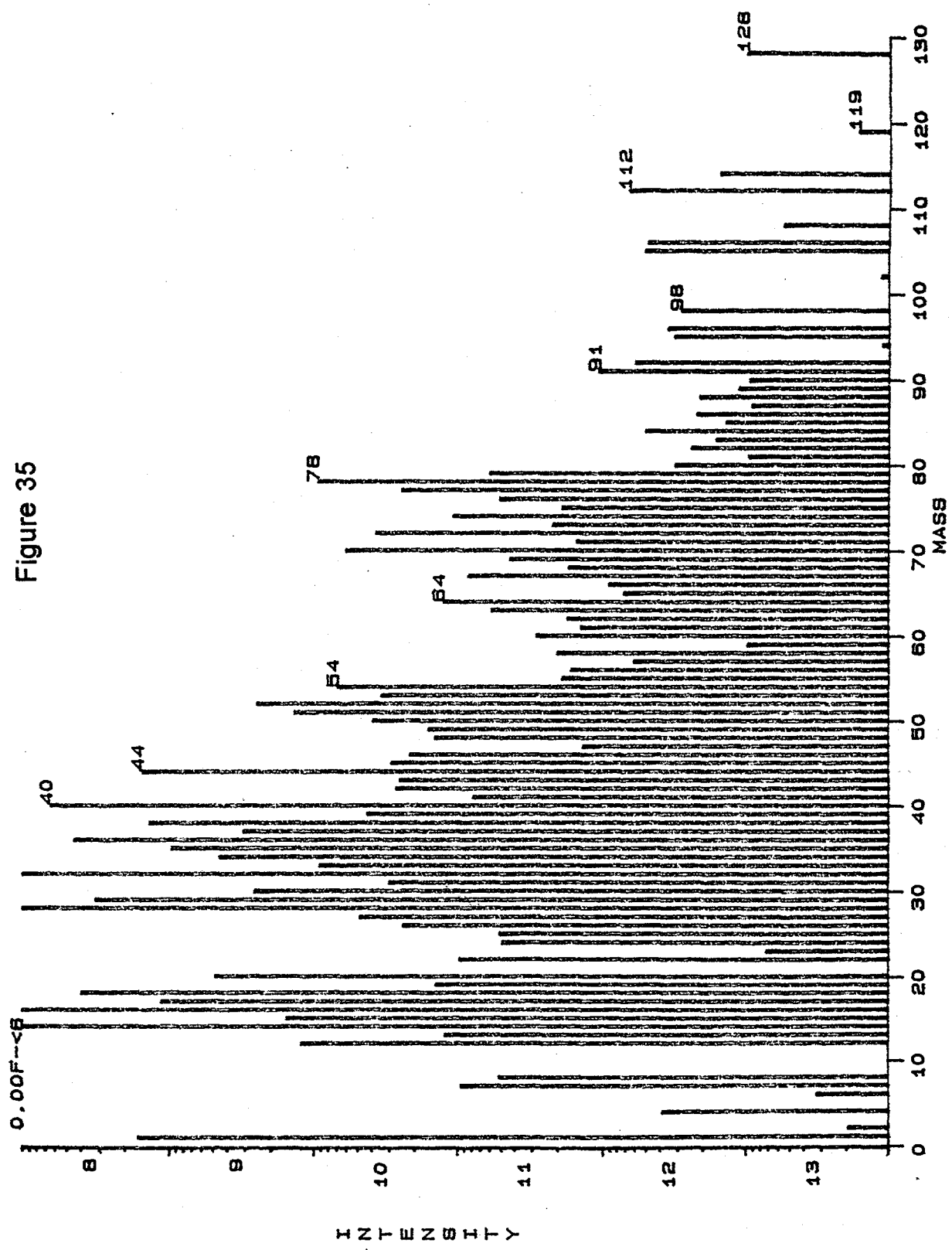
30-Dec-94

21: 55 26-May-95

File: 03P25N25

Scan: 70

Time: 00:27:57

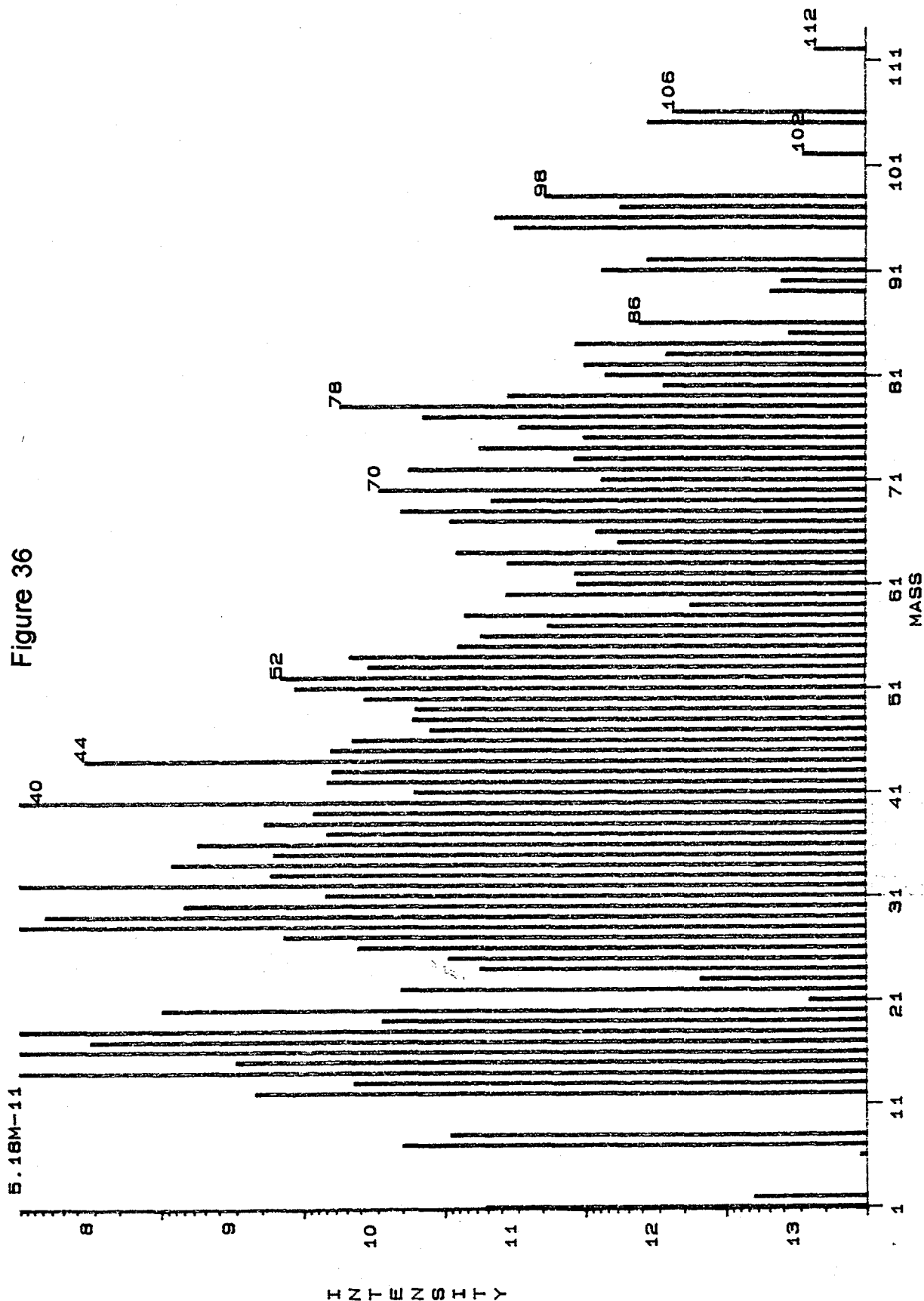


31-Dec-94

Created: 10:38:05

Cursor = 0

A1: -0.02 A2:



LC: 00:00:14

File: 73PVC50M

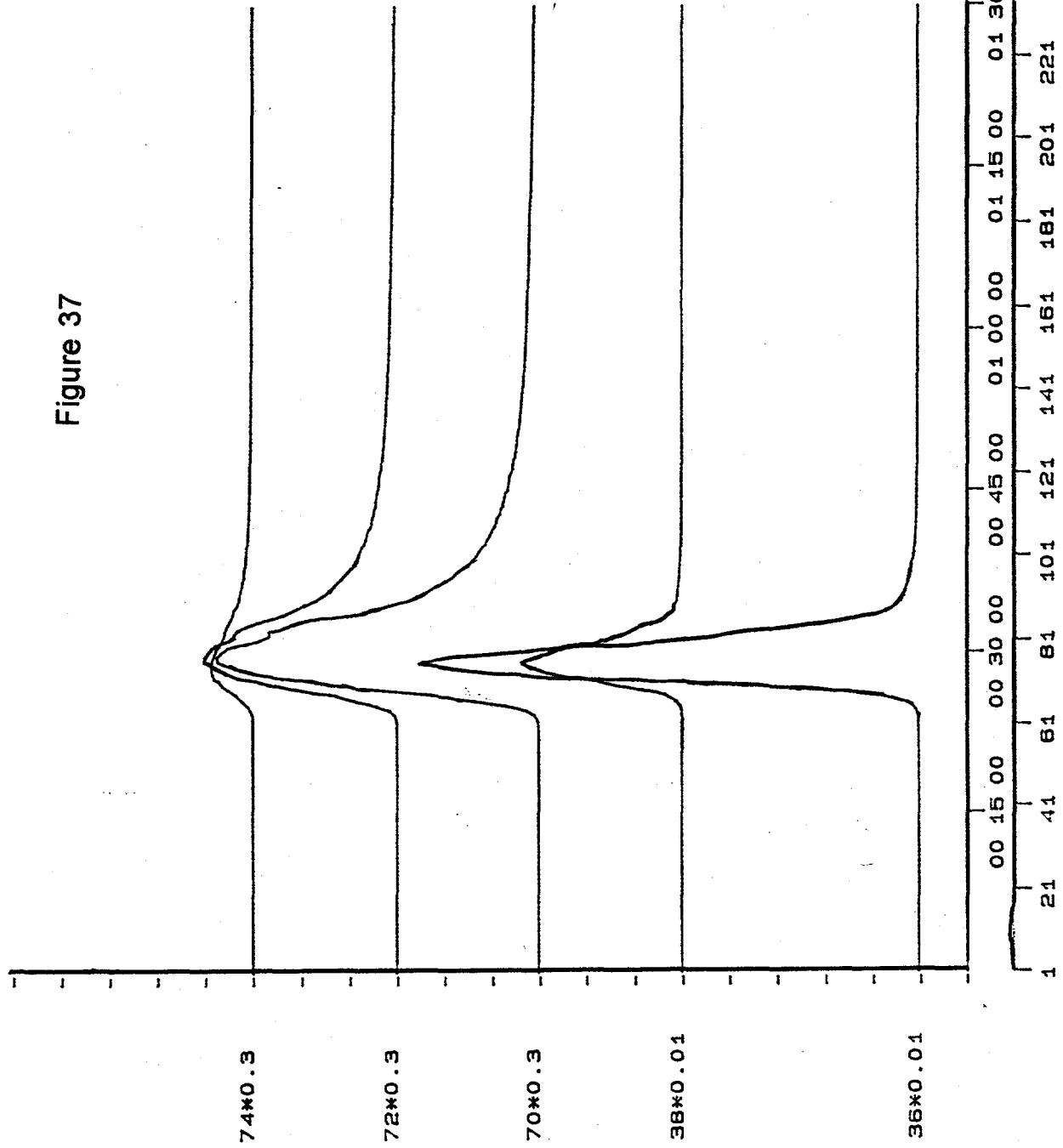
09:12 28-May-95

No: 1

Profile: BLANK

74*0.3	0.00M-20
72*0.3	1.51M-13
70*0.3	4.04M-13
38*0.01	6.12M-13
36*0.01	1.65M-12

Figure 37



08:52 28-May-95

File: 73P25N25

Scan: 1

LC: 00:00:14

Profile: BLANK

74*0.2

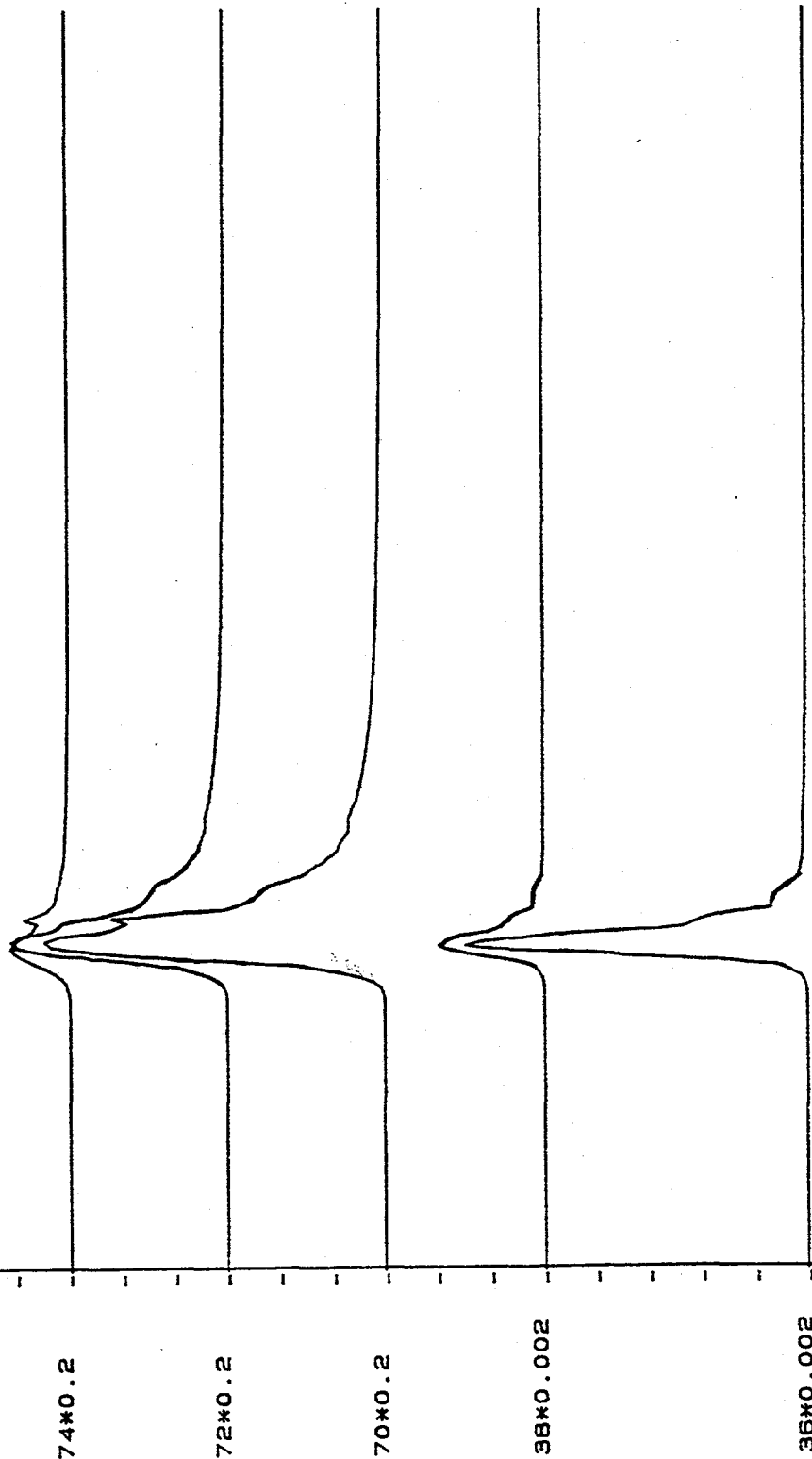
72*0.2

70*0.2

38*0.002

36*0.002

Figure 38



Time (h m s)

Scan No

Created: 19:48:16 12-Jan-95

LC: 00:00:12 Scan: 1 File: 735122

OB: 41 28-May-95

Profile: BLANK

74

72

70

38*0.05

36*0.05

Figure 39

74

72

70

38*0.05

36*0.05

Time (m s)

Scan No

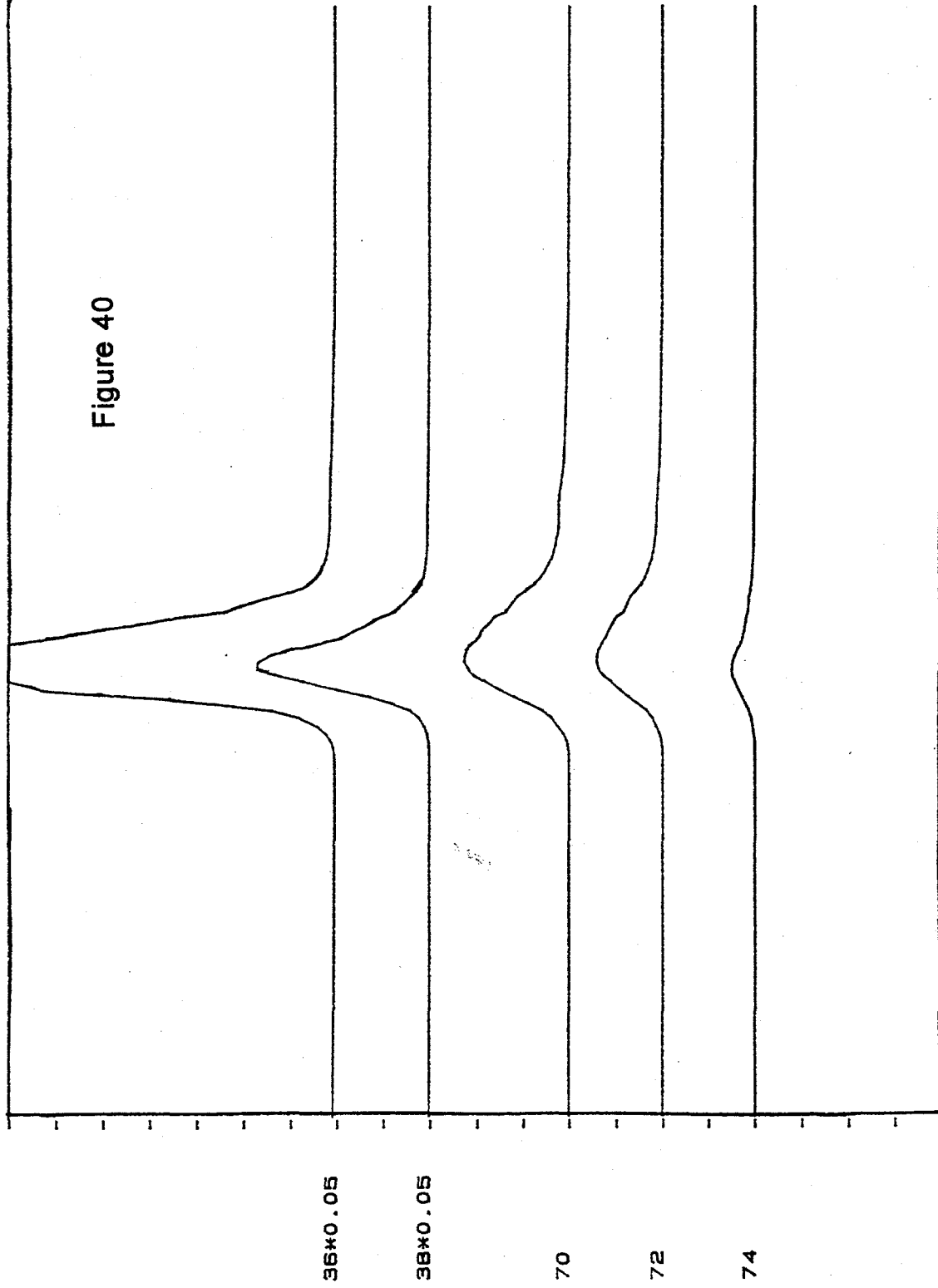
Time (m s)	Scan No
00 15 00	1
00 30 00	21
00 45 00	41
01 00 00	61
01 15 00	81
01 30 00	101
01 45 00	121
02 00 00	141
02 15 00	161
02 30 00	181
02 45 00	201
03 00 00	221

Created: 10:19:48

17-Jan-95

LC: 00:00:09 Scan: 1 File: 03PVC50 11:37 27-May-95

Profile: BLANK



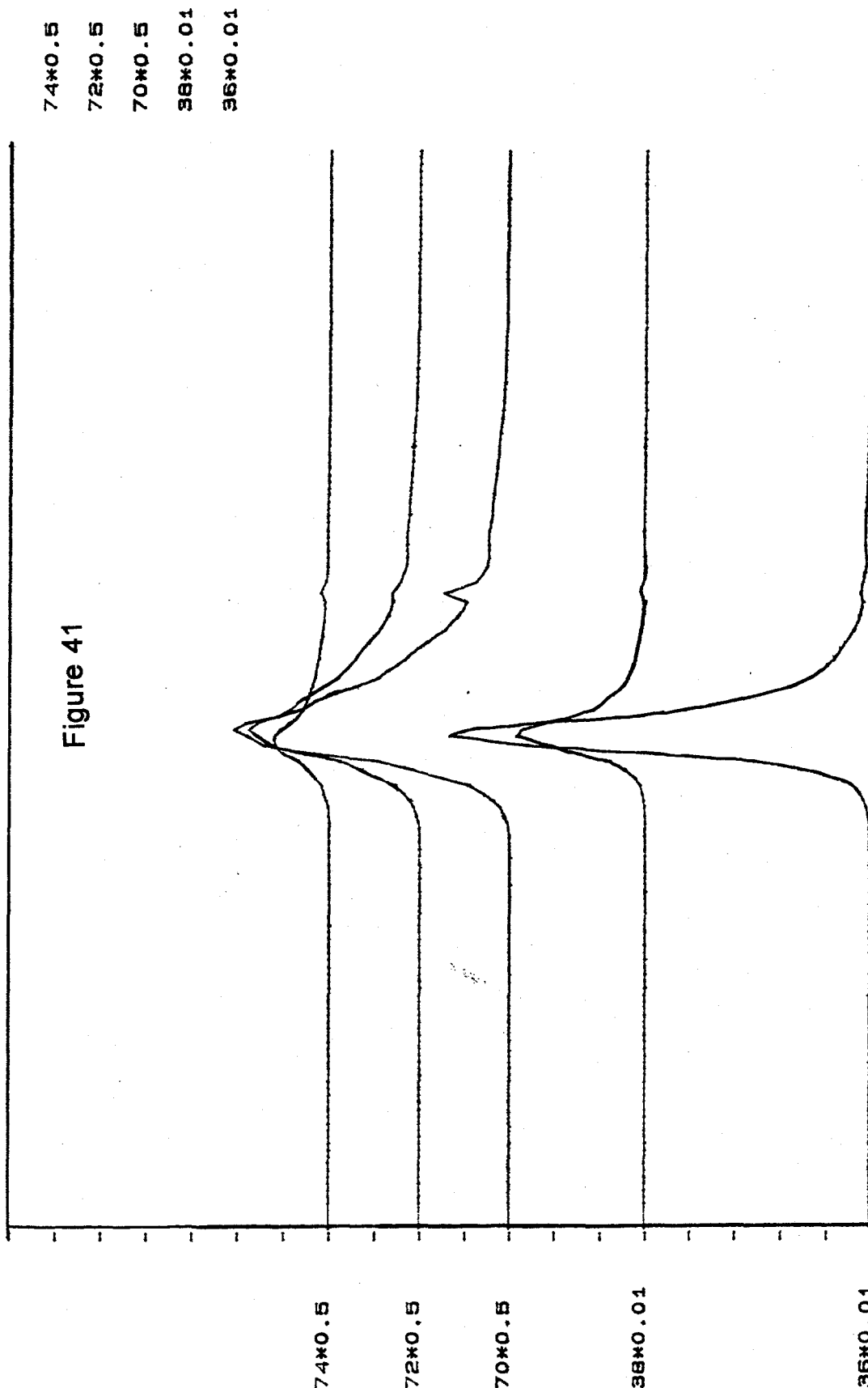
Time (h m s) 00 10 00 00 20 00 00 30 00 00 40 00 00 50 00 01 00 00

Temp (Deg C) 25 100 200 300 400 500 600 713

Created: 11:51:51 30-Dec-94

LC: 00:00:08 Scan: 1 File: 03P25N25 08:32 28-May-95

Profile: blank

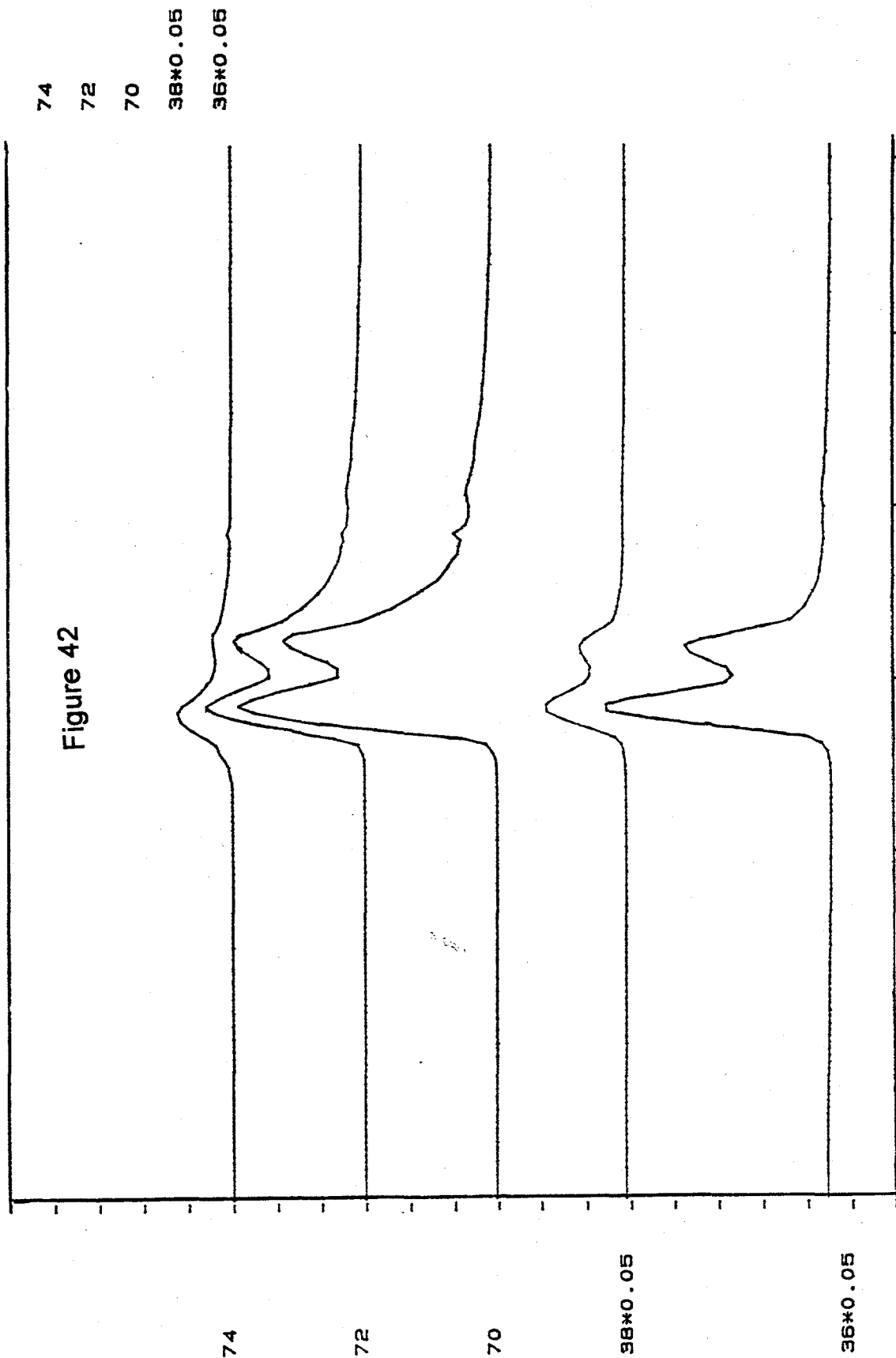


Time (h m s)	Scan No
00 08 00	11
00 16 00	21
00 24 00	31
00 32 00	41
00 40 00	51
00 48 00	61
00 56 00	71
01 04 00	81
01 12 00	91
01 20 00	101
01 28 00	111
01 36 00	121
01 44 00	131
01 52 00	141
02 00 00	151

Created: 11:08:54 31-Dec-94

LC: 00:00:08 Scan: 1 File: 035122 08:22 28-May-95

Profile: blank



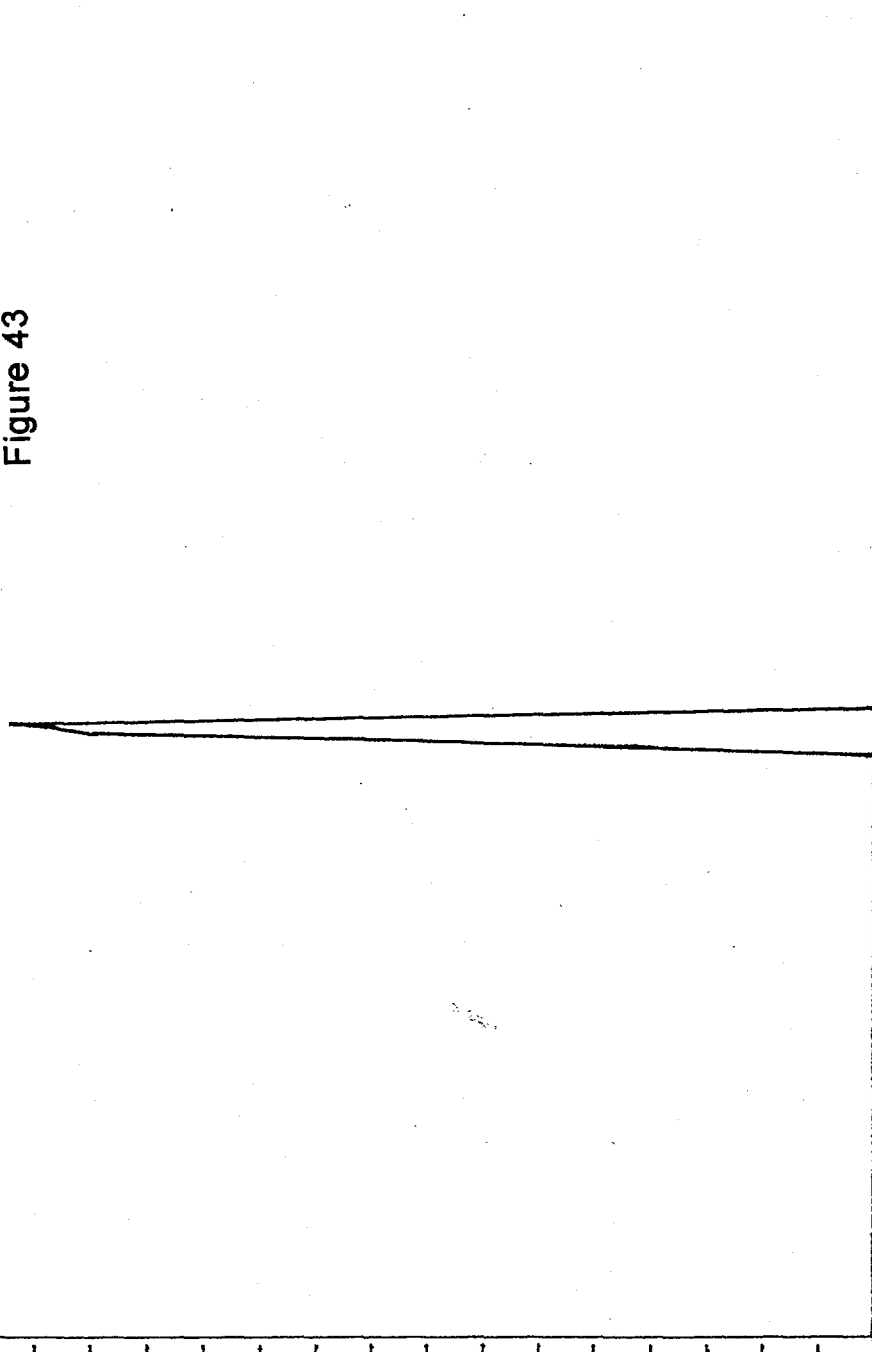
1 21 41 61 81 101 121 141
Created: 10:44:17 04-Jan-95

LC: 00:00:08 Scan: 1 File: 03B122 16:48 29-May-95

Profile: BLANKLI2

112*1500

Figure 43



112*1500

25 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900 2000 2100 2200 2300 2400 2500 2600 2700 2800 2900 3000 3100 3200 3300 3400 3500 3600 3700 3800 3900 4000 4100 4200 4300 4400 4500 4600 4700 4800 4900 5000 5100 5200 5300 5400 5500 5600 5700 5800 5900 6000 6100 6200 6300 6400 6500 6600 6700 6800 6900 7000 7100 7200 7300 7400 7500 7600 7700 7800 7900 8000 8100 8200 8300 8400 8500 8600 8700 8800 8900 9000 9100 9200 9300 9400 9500 9600 9700 9800 9900 10000 10100 10200 10300 10400 10500 10600 10700 10800 10900 11000 11100 11200 11300 11400 11500 11600 11700 11800 11900 12000 12100 12200 12300 12400 12500 12600 12700 12800 12900 13000 13100 13200 13300 13400 13500 13600 13700 13800 13900 14000 14100 14200 14300 14400 14500 14600 14700 14800 14900 15000 15100 15200 15300 15400 15500 15600 15700 15800 15900 16000 16100 16200 16300 16400 16500 16600 16700 16800 16900 17000 17100 17200 17300 17400 17500 17600 17700 17800 17900 18000 18100 18200 18300 18400 18500 18600 18700 18800 18900 19000 19100 19200 19300 19400 19500 19600 19700 19800 19900 20000 20100 20200 20300 20400 20500 20600 20700 20800 20900 21000 21100 21200 21300 21400 21500 21600 21700 21800 21900 22000 22100 22200 22300 22400 22500 22600 22700 22800 22900 23000 23100 23200 23300 23400 23500 23600 23700 23800 23900 24000 24100 24200 24300 24400 24500 24600 24700 24800 24900 25000 25100 25200 25300 25400 25500 25600 25700 25800 25900 26000 26100 26200 26300 26400 26500 26600 26700 26800 26900 27000 27100 27200 27300 27400 27500 27600 27700 27800 27900 28000 28100 28200 28300 28400 28500 28600 28700 28800 28900 29000 29100 29200 29300 29400 29500 29600 29700 29800 29900 30000 30100 30200 30300 30400 30500 30600 30700 30800 30900 31000 31100 31200 31300 31400 31500 31600 31700 31800 31900 32000 32100 32200 32300 32400 32500 32600 32700 32800 32900 33000 33100 33200 33300 33400 33500 33600 33700 33800 33900 34000 34100 34200 34300 34400 34500 34600 34700 34800 34900 35000 35100 35200 35300 35400 35500 35600 35700 35800 35900 36000 36100 36200 36300 36400 36500 36600 36700 36800 36900 37000 37100 37200 37300 37400 37500 37600 37700 37800 37900 38000 38100 38200 38300 38400 38500 38600 38700 38800 38900 39000 39100 39200 39300 39400 39500 39600 39700 39800 39900 40000 40100 40200 40300 40400 40500 40600 40700 40800 40900 41000 41100 41200 41300 41400 41500 41600 41700 41800 41900 42000 42100 42200 42300 42400 42500 42600 42700 42800 42900 43000 43100 43200 43300 43400 43500 43600 43700 43800 43900 44000 44100 44200 44300 44400 44500 44600 44700 44800 44900 45000 45100 45200 45300 45400 45500 45600 45700 45800 45900 46000 46100 46200 46300 46400 46500 46600 46700 46800 46900 47000 47100 47200 47300 47400 47500 47600 47700 47800 47900 48000 48100 48200 48300 48400 48500 48600 48700 48800 48900 49000 49100 49200 49300 49400 49500 49600 49700 49800 49900 50000 50100 50200 50300 50400 50500 50600 50700 50800 50900 51000 51100 51200 51300 51400 51500 51600 51700 51800 51900 52000 52100 52200 52300 52400 52500 52600 52700 52800 52900 53000 53100 53200 53300 53400 53500 53600 53700 53800 53900 54000 54100 54200 54300 54400 54500 54600 54700 54800 54900 55000 55100 55200 55300 55400 55500 55600 55700 55800 55900 56000 56100 56200 56300 56400 56500 56600 56700 56800 56900 57000 57100 57200 57300 57400 57500 57600 57700 57800 57900 58000 58100 58200 58300 58400 58500 58600 58700 58800 58900 59000 59100 59200 59300 59400 59500 59600 59700 59800 59900 60000 60100 60200 60300 60400 60500 60600 60700 60800 60900 61000 61100 61200 61300 61400 61500 61600 61700 61800 61900 62000 62100 62200 62300 62400 62500 62600 62700 62800 62900 63000 63100 63200 63300 63400 63500 63600 63700 63800 63900 64000 64100 64200 64300 64400 64500 64600 64700 64800 64900 65000 65100 65200 65300 65400 65500 65600 65700 65800 65900 66000 66100 66200 66300 66400 66500 66600 66700 66800 66900 67000 67100 67200 67300 67400 67500 67600 67700 67800 67900 68000 68100 68200 68300 68400 68500 68600 68700 68800 68900 69000 69100 69200 69300 69400 69500 69600 69700 69800 69900 70000 70100 70200 70300 70400 70500 70600 70700 70800 70900 71000 71100 71200 71300 71400 71500 71600 71700 71800 71900 72000 72100 72200 72300 72400 72500 72600 72700 72800 72900 73000 73100 73200 73300 73400 73500 73600 73700 73800 73900 74000 74100 74200 74300 74400 74500 74600 74700 74800 74900 75000 75100 75200 75300 75400 75500 75600 75700 75800 75900 76000 76100 76200 76300 76400 76500 76600 76700 76800 76900 77000 77100 77200 77300 77400 77500 77600 77700 77800 77900 78000 78100 78200 78300 78400 78500 78600 78700 78800 78900 79000 79100 79200 79300 79400 79500 79600 79700 79800 79900 80000 80100 80200 80300 80400 80500 80600 80700 80800 80900 81000 81100 81200 81300 81400 81500 81600 81700 81800 81900 82000 82100 82200 82300 82400 82500 82600 82700 82800 82900 83000 83100 83200 83300 83400 83500 83600 83700 83800 83900 84000 84100 84200 84300 84400 84500 84600 84700 84800 84900 85000 85100 85200 85300 85400 85500 85600 85700 85800 85900 86000 86100 86200 86300 86400 86500 86600 86700 86800 86900 87000 87100 87200 87300 87400 87500 87600 87700 87800 87900 88000 88100 88200 88300 88400 88500 88600 88700 88800 88900 89000 89100 89200 89300 89400 89500 89600 89700 89800 89900 90000 90100 90200 90300 90400 90500 90600 90700 90800 90900 91000 91100 91200 91300 91400 91500 91600 91700 91800 91900 92000 92100 92200 92300 92400 92500 92600 92700 92800 92900 93000 93100 93200 93300 93400 93500 93600 93700 93800 93900 94000 94100 94200 94300 94400 94500 94600 94700 94800 94900 95000 95100 95200 95300 95400 95500 95600 95700 95800 95900 96000 96100 96200 96300 96400 96500 96600 96700 96800 96900 97000 97100 97200 97300 97400 97500 97600 97700 97800 97900 98000 98100 98200 98300 98400 98500 98600 98700 98800 98900 99000 99100 99200 99300 99400 99500 99600 99700 99800 99900 100000 100100 100200 100300 100400 100500 100600 100700 100800 100900 101000 101100 101200 101300 101400 101500 101600 101700 101800 101900 102000 102100 102200 102300 102400 102500 102600 102700 102800 102900 103000 103100 103200 103300 103400 103500 103600 103700 103800 103900 104000 104100 104200 104300 104400 104500 104600 104700 104800 104900 105000 105100 105200 105300 105400 105500 105600 105700 105800 105900 106000 106100 106200 106300 106400 106500 106600 106700 106800 106900 107000 107100 107200 107300 107400 107500 107600 107700 107800 107900 108000 108100 108200 108300 108400 108500 108600 108700 108800 108900 109000 109100 109200 109300 109400 109500 109600 109700 109800 109900 110000 110100 110200 110300 110400 110500 110600 110700 110800 110900 111000 111100 111200 111300 111400 111500 111600 111700 111800 111900 112000 112100 112200 112300 112400 112500 112600 112700 112800 112900 113000 113100 113200 113300 113400 113500 113600 113700 113800 113900 114000 114100 114200 114300 114400 114500 114600 114700 114800 114900 115000 115100 115200 115300 115400 115500 115600 115700 115800 115900 116000 116100 116200 116300 116400 116500 116600 116700 116800 116900 117000 117100 117200 117300 117400 117500 117600 117700 117800 117900 118000 118100 118200 118300 118400 118500 118600 118700 118800 118900 119000 119100 119200 119300 119400 119500 119600 119700 119800 119900 120000 120100 120200 120300 120400 120500 120600 120700 120800 120900 121000 121100 121200 121300 121400 121500 121600 121700 121800 121900 122000 122100 122200 122300 122400 122500 122600 122700 122800 122900 123000 123100 123200 123300 123400 123500 123600 123700 123800 123900 124000 124100 124200 124300 124400 124500 124600 124700 124800 124900 125000 125100 125200 125300 125400 125500 125600 125700 125800 125900 126000 126100 126200 126300 126400 126500 126600 126700 126800 126900 127000 127100 127200 127300 127400 127500 127600 127700 127800 127900 128000 128100 128200 128300 128400 128500 128600 128700 128800 128900 129000 129100 129200 129300 129400 129500 129600 129700 129800 129900 130000 130100 130200 130300 130400 130500 130600 130700 130800 130900 131000 131100 131200 131300 131400 131500 131600 131700 131800 131900 132000 132100 132200 132300 132400 132500 132600 132700 132800 132900 133000 133100 133200 133300 133400 133500 133600 133700 133800 133900 134000 134100 134200 134300 134400 134500 134600 134700 134800 134900 135000 135100 135200 135300 135400 135500 135600 135700 135800 135900 136000 136100 136200 136300 136400 136500 136600 136700 136800 136900 137000 137100 137200 137300 137400 137500 137600 137700 137800 137900 138000 138100 138200 138300 138400 138500 138600 138700 138800 138900 139000 139100 139200 139300 139400 139500 139600 139700 139800 139900 140000 140100 140200 140300 140400 140500 140600 140700 140800 140900 141000 141100 141200 141300 141400 141500 141600 141700 141800 141900 142000 142100 142200 142300 142400 142500 142600 142700 142800 142900 143000 143100 143200 143300 143400 143500 143600 143700 143800 143900 144000 144100 144200 144300 144400 144500 144600 144700 144800 144900 145000 145100 145200 145300 145400 145500 145600 145700 145800 145900 146000 146100 146200 146300 146400 146500 146600 146700 146800 146900 147000 147100 147200 147300 147400 147500 147600 147700 147800 147900 148000 148100 148200 148300 148400 148500 148600 148700 148800 148900 149000 149100 149200 149300 149400 149500 149600 149700 149800 149900 150000 150100 150200 150300 150400 150500 150600 150700 150800 150900 151000 151100 151200 151300 151400 151500 151600 151700 151800 151900 152000 152100 152200 152300 152400 152500 152600 152700 152800 152900 153000 153100 153200 153300 153400 153500 153600 153700 153800 153900 154000 154100 154200 154300 154400 154500 154600 154700 154800 154900 155000 155100 155200 155300 155400 155500 155600 155700 155800 155900 156000 156100 156200 156300 156400 156500 156600 156700 156800 156900 157000 157100 157200 157300 157400 157500 157600 157700 157800 157900 158000 158100 158200 158300 158400 158500 158600 158700 158800 158900 159000 159100 159200 159300 159400 159500 159600 159700 159800 159900 160000 160100 160200 160300 160400 160500 160600 160700 160800 160900 161000 161100 161200 161300 161400 161500 161600 161700 161800 161900 162000 162100 162200 162300 162400 162500 162600 162700 162800 162900 163000 163100 163200 163300 163400 163500 163600 163700 163800 163900 164000 164100 164200 164300 164400 164500 164600 164700 164800 164900 165000 165100 165200 165300 165400 165500 165600 165700 165800 165900 166000 166100 166200 166300 166400 166500 166600 166700 166800 166900 167000 167100 167200 167300 167400 167500 167600 167700 167800 167900 168000 168100 168200 168300 168400 168500 168600 168700 168800 168900 169000 169100 169200 169300 169400 169500 169600 169700 169800 169900 170000 170100 170200 170300 170400 170500 170600 170700 170800 170900 171000 171100 171200 171300 171400 171500 171600 171700 171800 171900 172000 172100 172200 172300 172400 172500 172600 172700 172800 172900 173000 173100 173200 173300 173400 173500 173600 173700 173800 173900 174000 174100 174200 174300 174400 174500 174600 174700 174800 174900 175000 175100 175200 175300 175400 175500 175600 175700 175800 175900 176000 176100 176200 176300 176400 176500 176600 176700 176800 176900 177000 177100 177200 177300 177400 177500 177600 177700 177800 177900 178000 178100 178200 178300 178400 178500 178600 178700 178800 178900 179000 179100 179200 179300 179400 179500 179600 179700 179800 179900 180000 180100 180200 180300 180400 180500 180600 180700 180800 180900 181000 181100 181200 181300 181400 181500 181600 181700 181800 181900 182000 182100 182200 182300 182400 182500 182600 182700 182800 182900 183000 183100 183200 183300 183400 183500 183600 183700 183800 183900 184000 184100 184200 184300 184400 184500 184600 184700 184800 184900 185000 185100 185200 185300 185400 185500 185600 185700 185800 185900 186000 186100 186200 186300 186400 186500 18

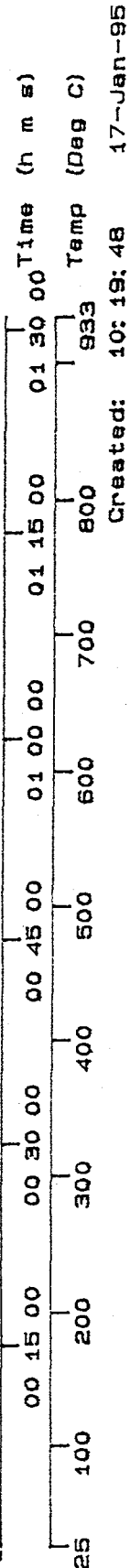
LC: 00: 00: 12 Scan: 1 File: 735122 16: 43 29-May-95

Profile: BLANKLI2

112*150

Figure 44

112*150



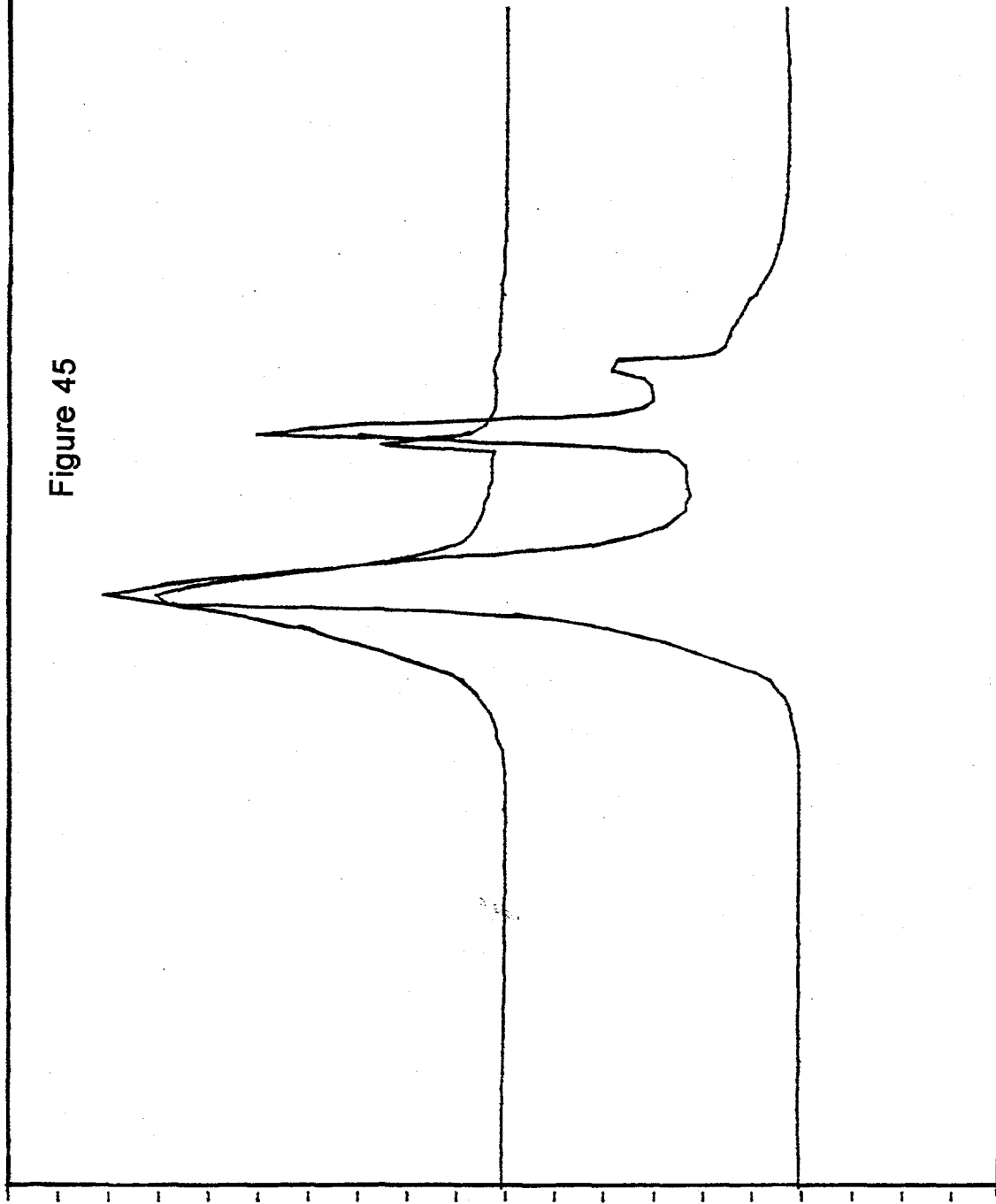
LC: 00:00:06 Scan: 1 File: 035122 09:24 28-May-95

Profile: BLANK1

60*5

64*2

Figure 45



Time (h m s) 00 10 00 00 20 00 00 30 00 00 40 00 00 50 00 01 00 00
Temp (Deg C) 637 500 400 300 200 100 25

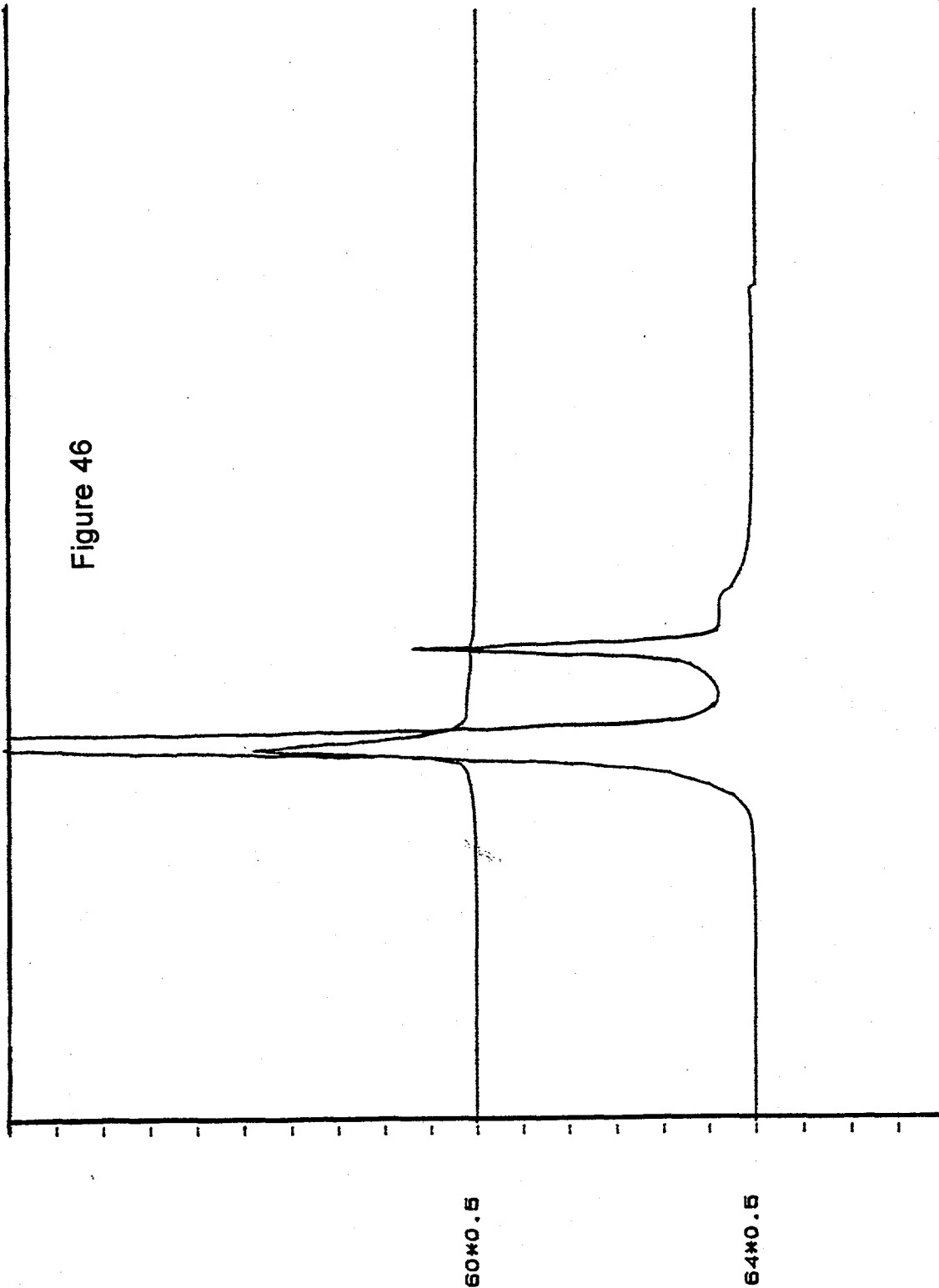
Created: 10:44:17 04-Jan-95

LC: 00:00:12 Scan: 1 File: 735122 09:33 28-May-95

Profile: BLANK1

60x0.5
64x0.5

Figure 46



Time (h m s) 01 30 00 01 15 00 01 00 00 00 45 00 00 30 00 00 15 00 00 00 00
Temp (Deg C) 933 800 700 600 500 400 300 200 100 25
Created: 10:19:48 17-Jan-95

CO2 O2 Concentration (GC)

April 25, 1995 Combustion

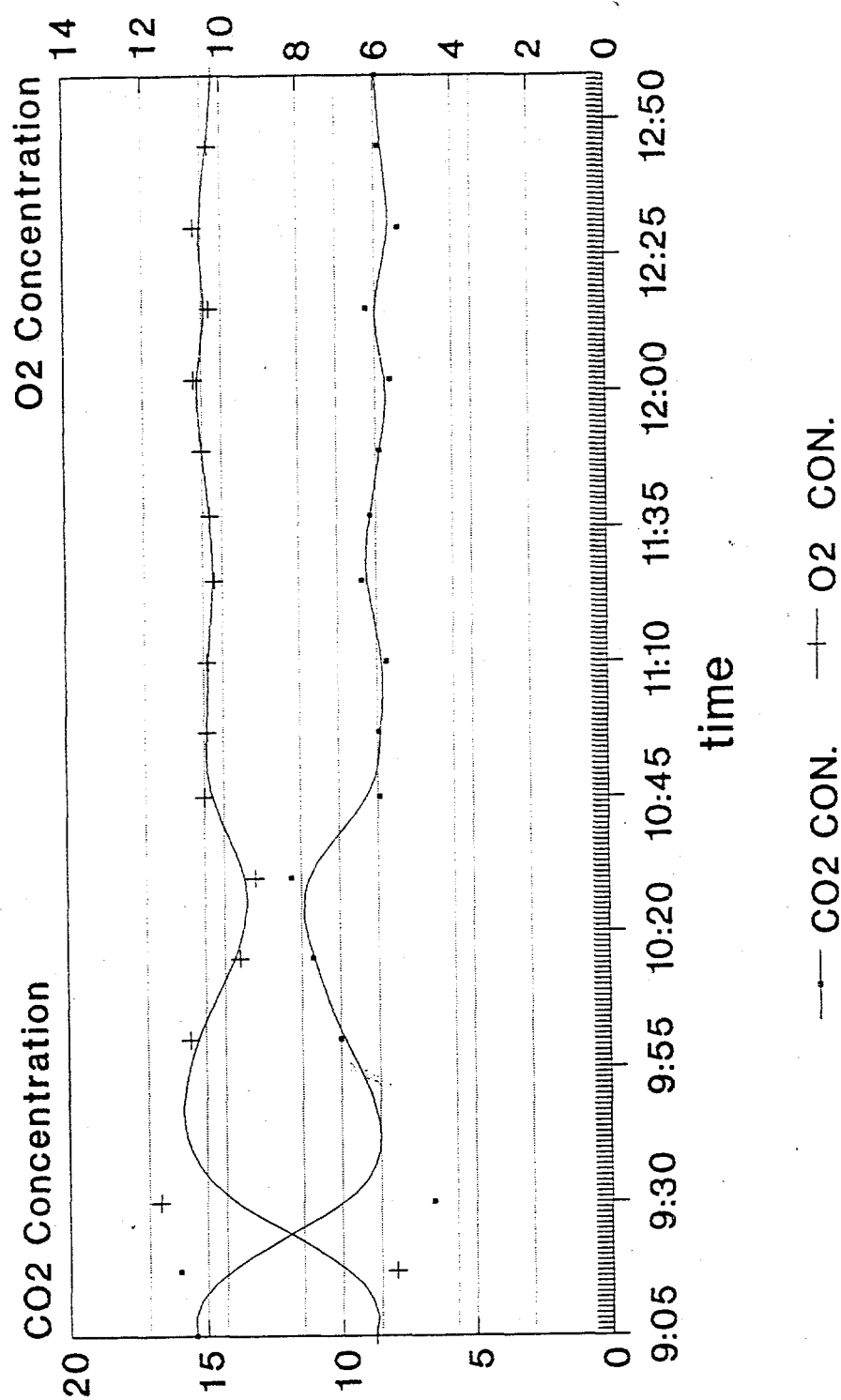


Figure 47

CO2 O2 Concentration (GC)

April 25, 1995 Combustion

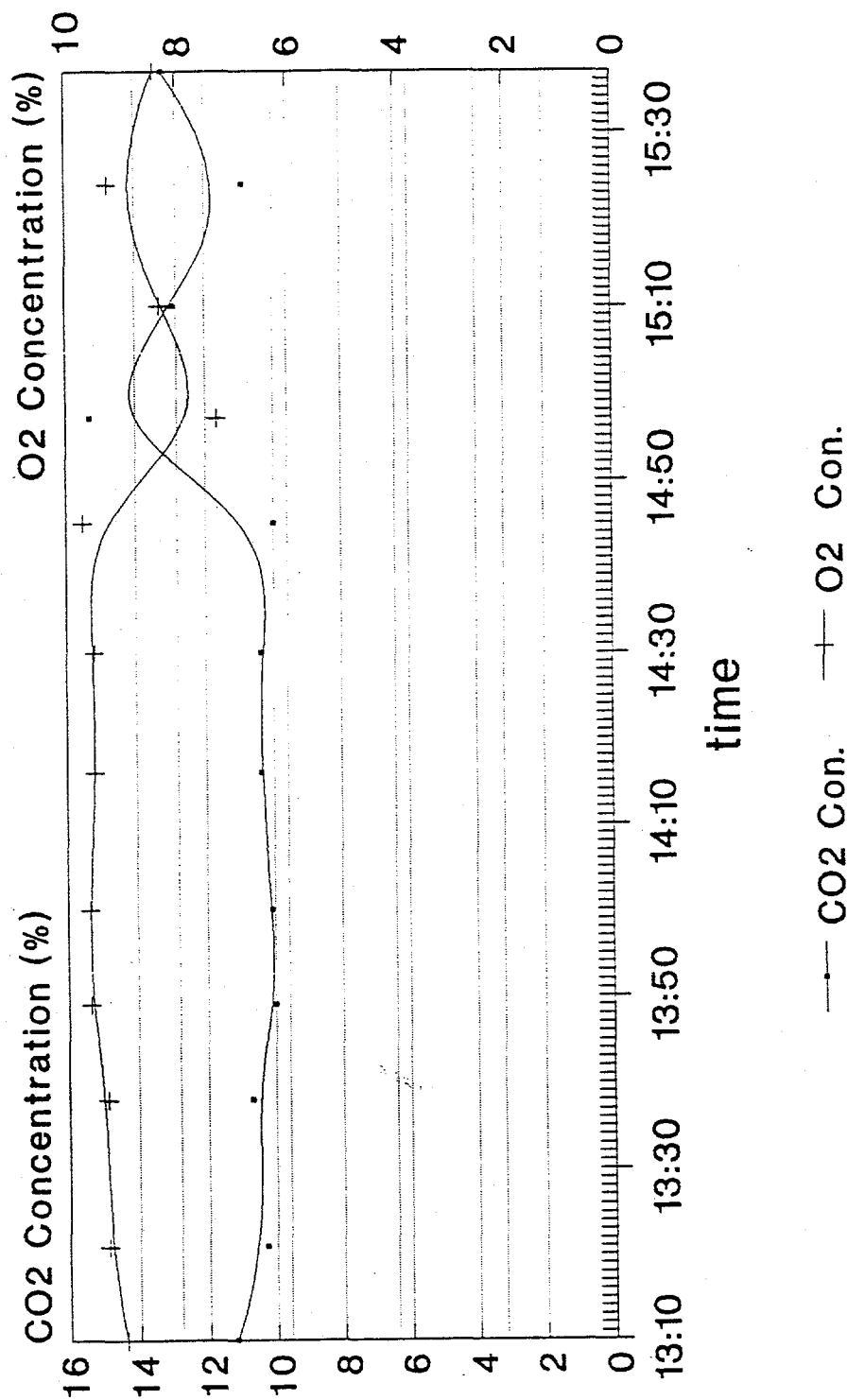


Figure 48

Bed Temperature (°F) with time

April 25, 1995 Combustion

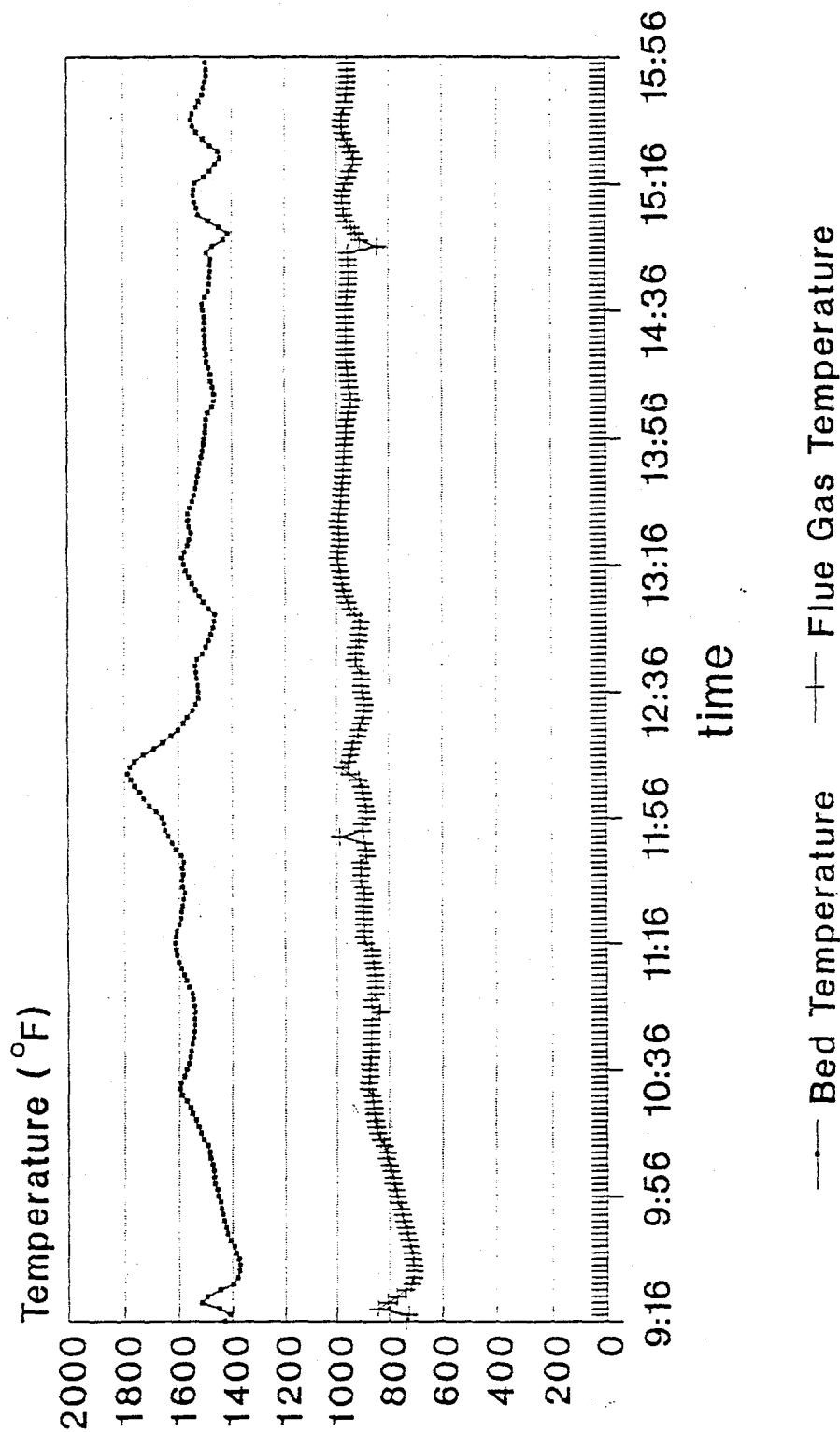


Figure 49

CO₂, O₂ Concentration (GC)

May 10, 1995 Combustion

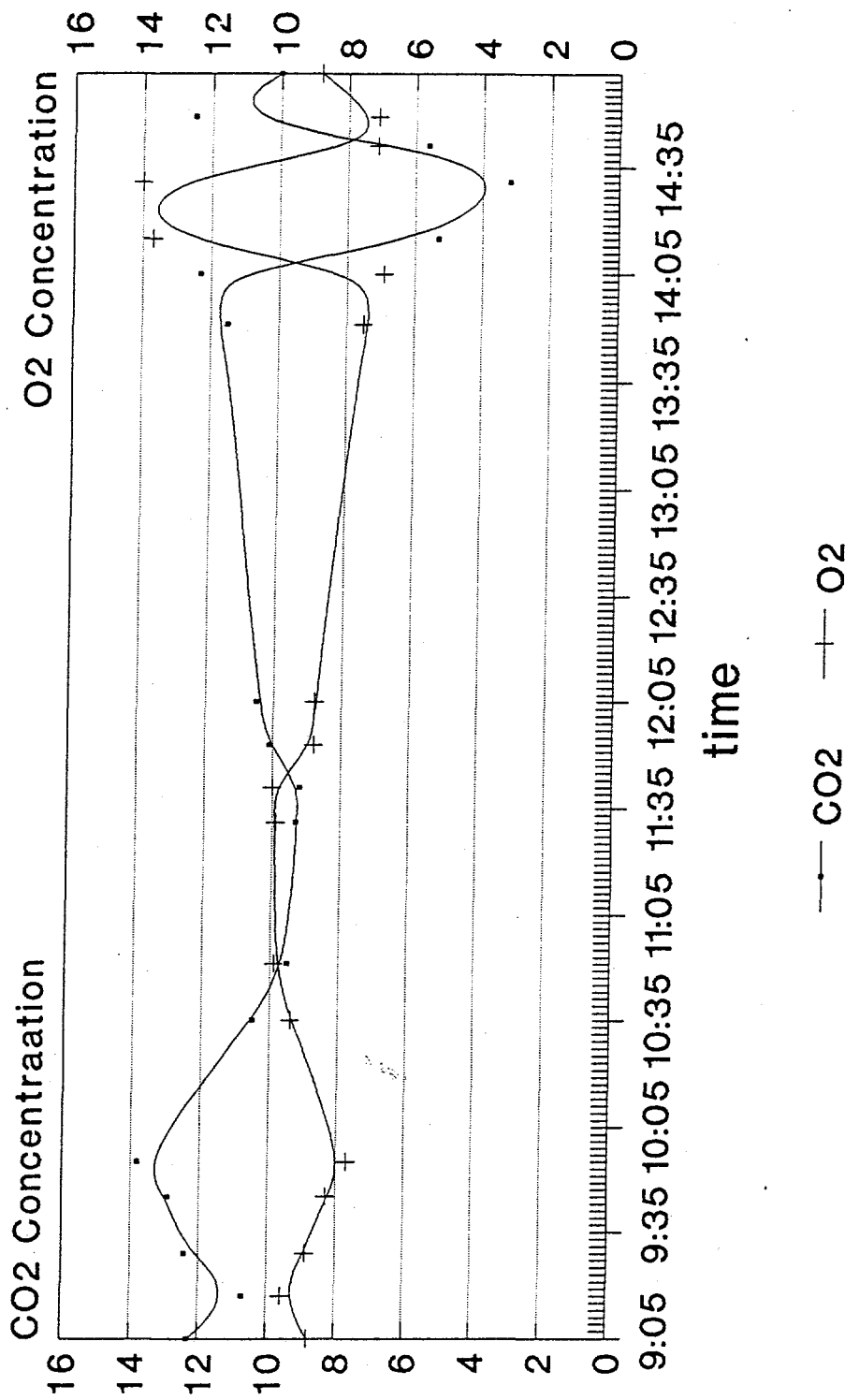


Figure 50

Bed Temperature(°F) with time

May 10 '95 Combustion

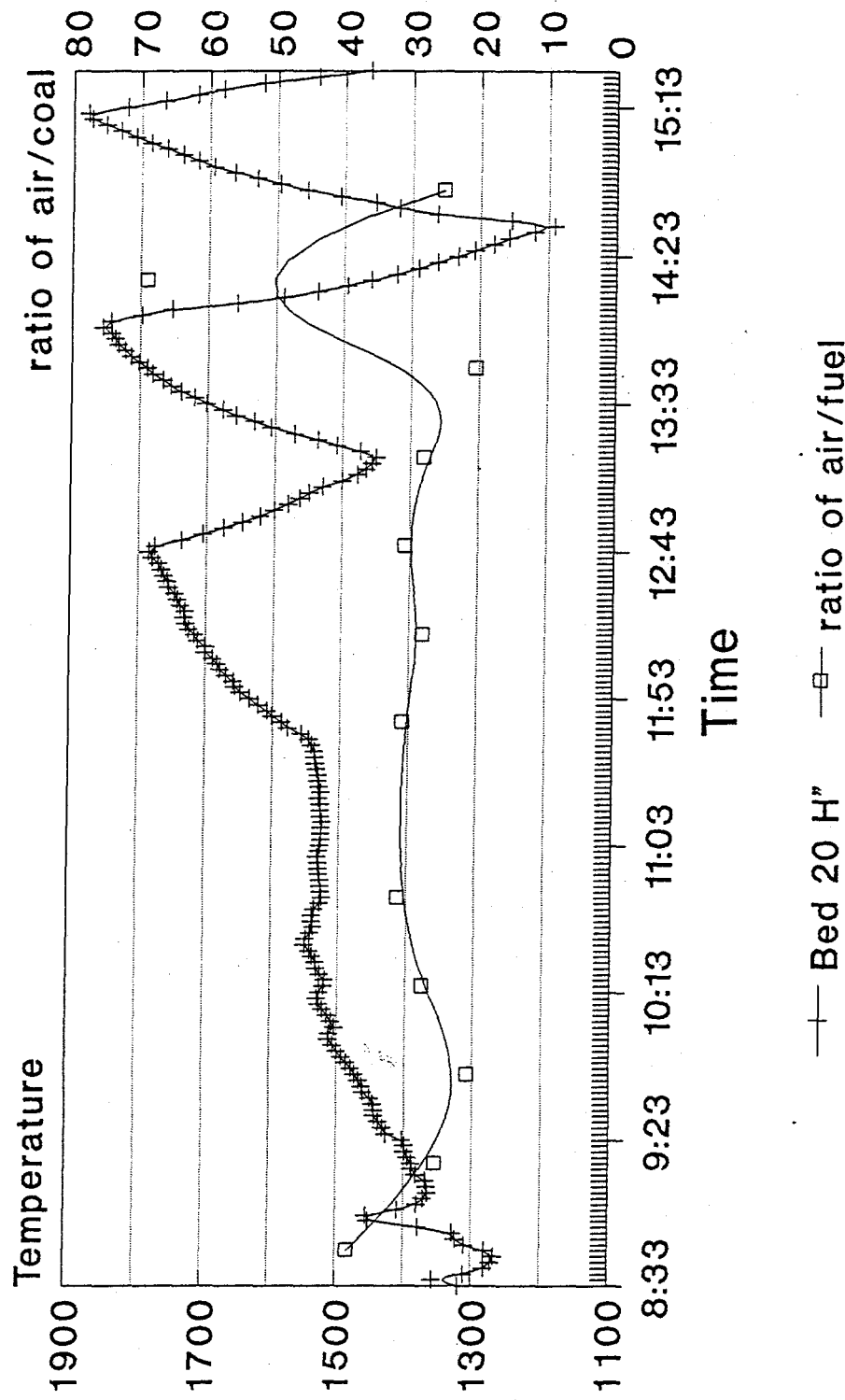


Figure 51