"Technical Studies on Asphalt," Report No. 1

State Study No. 83-02-2

SPECTRAL ANALYSES

of

HOT RECYCLING AGENTS

by

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EXECUTIVE SUMMARY

This report contains standardized baseline data for a series of Hot Recycling Agents and AC-3 asphalt. The hot recycling agents are identified by their RA number (RA-6, RA-25, RA-100 and RA-275) where the RA number is defined as the average viscosity of the sample at 140°F divided by 100. The recycling agents and the AC-3 have been characterized by solubility measurements to determine maltene, resin, and oil contents which have been compared to nuclear magnetic resonance (^{1}H and ^{13}C NMR) and infrared (IR) spectral data.

The RA numbers have been found to correlate with the resin/oil and high affinity/low affinity ratios, C-H stretching intensity ratios and ^{13}C-NMR intensity ratios. The data should form a basis for the identification of recycling agents.

Analyses of Hot Recycling Agents

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I. Introduction

This report contains standardized baseline data for a series of Hot Recycling Agents (RA-6, RA-25, RA-100, and RA-275) and AC-3. The data describes the chemical groupings as measured by maltene, resin, and oil content, as well as by nuclear magnetic resonance (NMR) and infrared (IR) spectral data.

II. Solubility Analyses (n-Pentane Separation Procedure)

The asphaltenes and maltenes are separated by pentane solubility. A rapid procedure has been developed which parallels the Hubbard-Stanfield determination of asphaltenes, oils, and resins.[1] A 1.00-gm. sample of the asphalt is shaken with 100 ml of n-pentane and then let stand for three hours. The mixture is gravity filtered. The insoluble material is designated as the asphaltenes and the soluble portion as maltenes. The maltenes are then absorbed on activated alumnia with n-pentane to remove the oils. The aluminia is then washed with solvent to remove the absorbed substances. In this work the aluminia is first washed with CS_2 to remove low affinity resins and then with tetrahydrofuran (THF) to remove the high affinity resins.

Figure 1 presents the data (Table 1) as a function of RA number, where the RA number is symbolic of the average viscosity of the sample at 140°F. The smoothness of the resin/oil curve implies that this ratio can be used to characterize the hot recycling agents. It would be important to obtain the same data for such materials from additional vendors to confirm the validity of this relationship.

The maltene measurement is repeatable with an error of less than 1%; however, while the oil and resin contents are reliable and repeatable for the RA samples with the asphalt samples an improved

Table 1

Solubility Analyses

Sample	% Pentane Soluble (Maltenes)	% Oils*	Resins*		Ratios	
			% HA	% LA	Res./Oils	HA/LA
RA-6	99.9	77.1	8.3	15.4	0.31	0.54
RA-25	97.7	58.3	14.5	24.9	0.68	0.58
RA-100	98.6	53.0	22.4	27.6	0.94	0.81
RA-275	98.9	50.2	24.7	27.9	1.05	0.89
AC-3	78.5	23.3	43.8	41.0	--	--
AC-4	84.7	23.5	48.5	32.8	--	--

* Oils and resins are reported as a percentage of the maltenes.

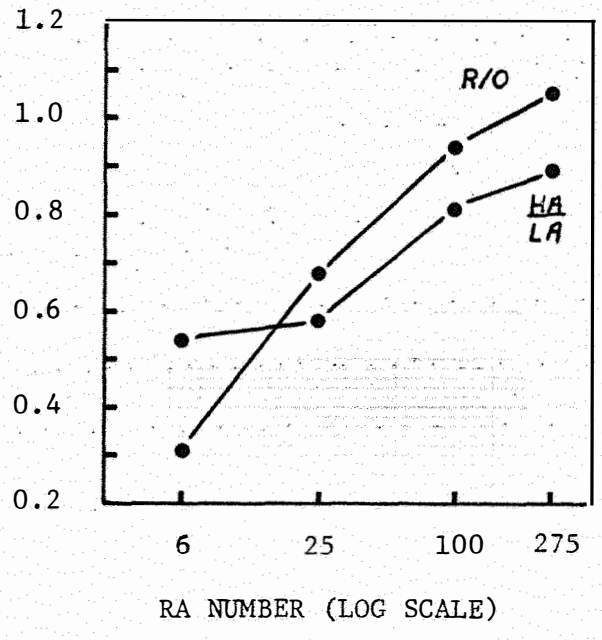


Figure 1: Solubility Analyses

technique will have to be developed or more sophisticated apparatus utilized.[1]

III. Infrared Spectra

The infrared spectra were recorded as thin films on KBr plates with the thickness of the film adjusted to give a tallest peak of 70% transmission to avoid saturation. The spectra for RA-6, RA-25, and RA-100 are too similar to obtain unique identification in the C-H stretching region (2900 cm^{-1}) and a peak at 1600 cm^{-1}. This latter peak might be assigned to a carbonyl grouping; however, it also could be due to unsaturation.

The infrared spectra (Figures 2-6) are almost identical. It would have been helpful to obtain an obtious trend with respect to the relative peak heights; however, no such trend is observed when the % transmission scale is used to present the data. When the Absorbance scale is used the spectra (Figures 7-10) appear to have different intensity ratios in the C-H stretching ratio. Indeed, when peak heights are used to quantitize the data the samples can be differentiated (Table 2).

The best way to differentiate these samples by infrared spectroscopy is to note that the RA numbers correlate well with the difficulty of obtaining a suitable film on a KBr disc. The RA-275 is the most difficult.

IV. Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance (NMR) data can be used to describe the chemical environment of the nucleus being examined. The ^{1}H spectra have essentially the same features for each hot recycling agent as well as for AC-3.

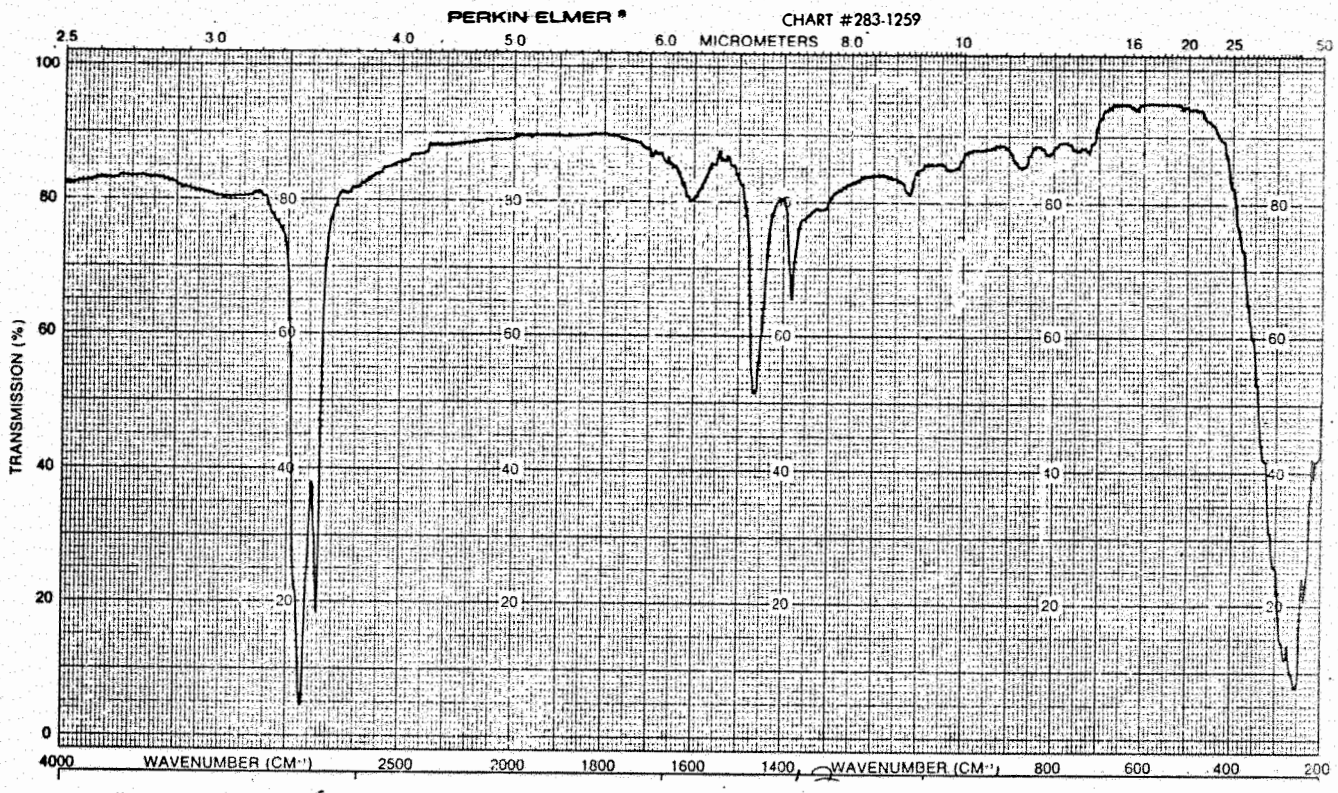


Figure 2: Infrared Spectrum of AC-3

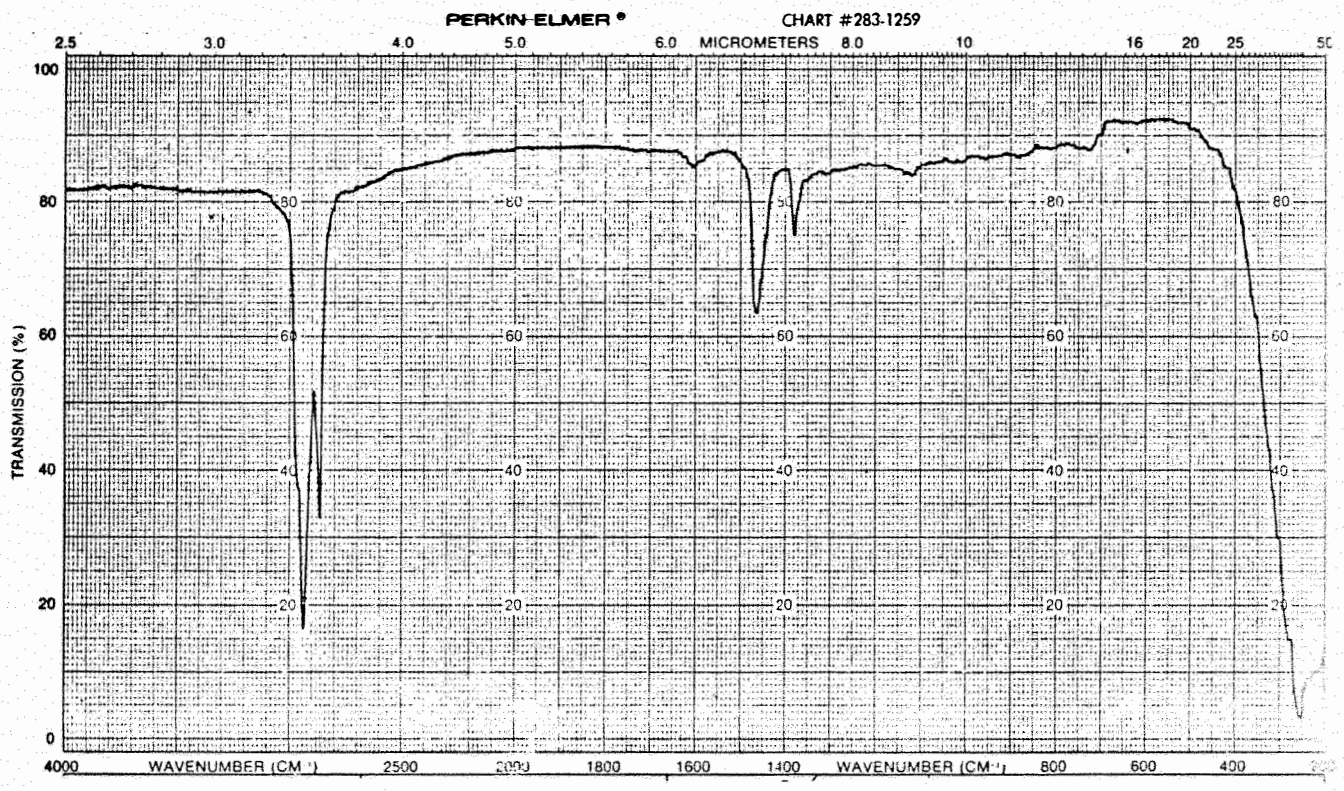


Figure 3: Infrared Spectrum of RA-6

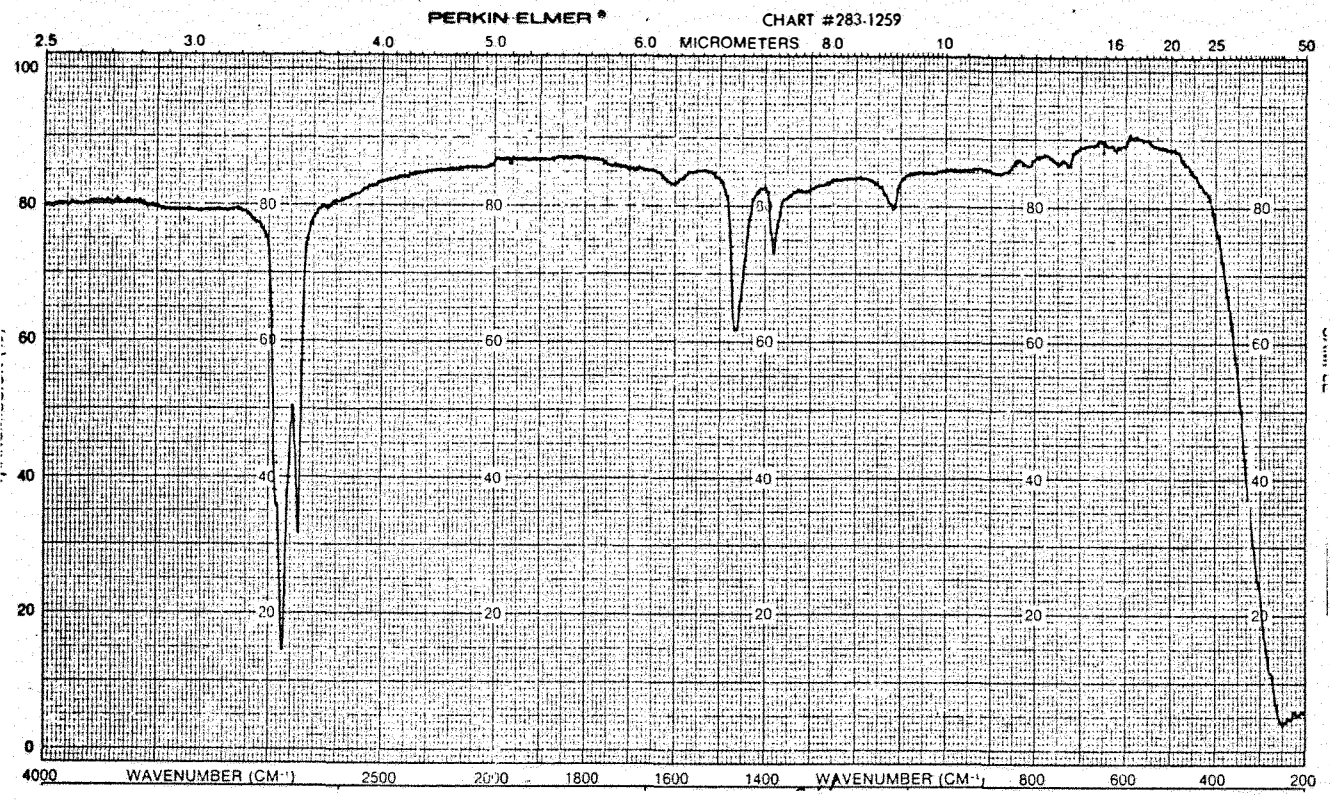


Figure 4: Infrared Spectrum of RA-25

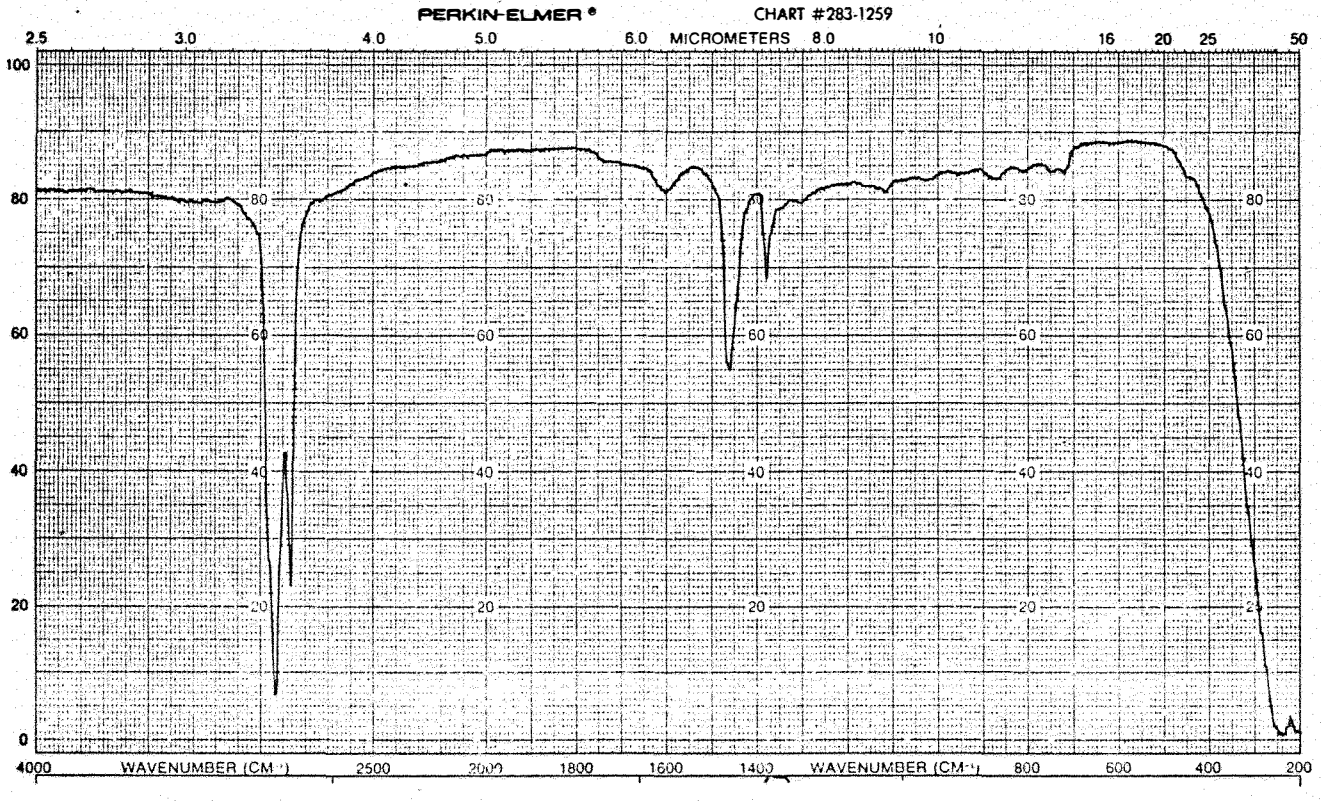


Figure 5: Infrared Spectrum of RA-100

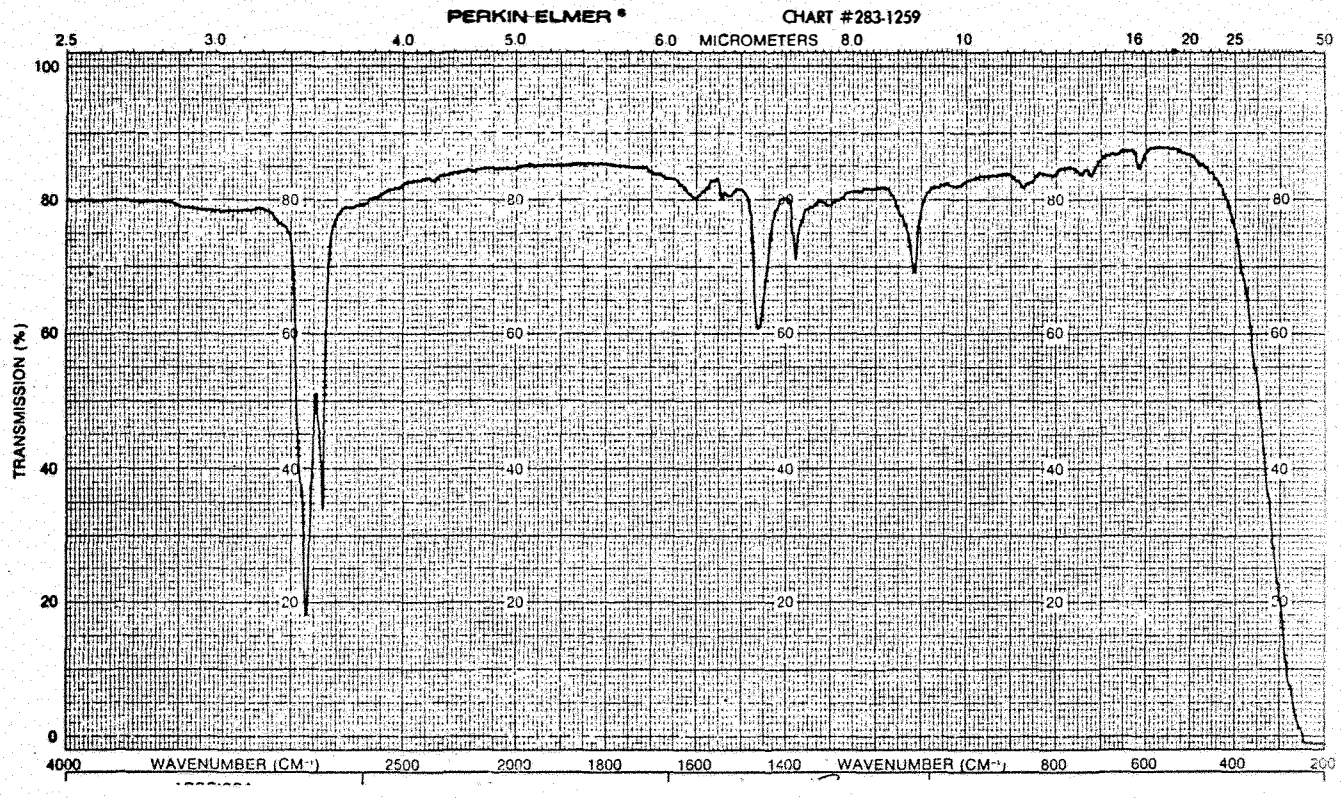


Figure 6: Infrared Spectrum of RA-275

Table 2

Relative Peak Intensities ν C-H (Absorbance Scale)

Sample	2960 cm^{-1}	2930 cm^{-1}	2860 cm^{-1}
RA-6	1	1.88	1.14
RA-25	1	1.94	1.13
RA-100	1	2.19	1.15
RA-275	1	2.17	0.60

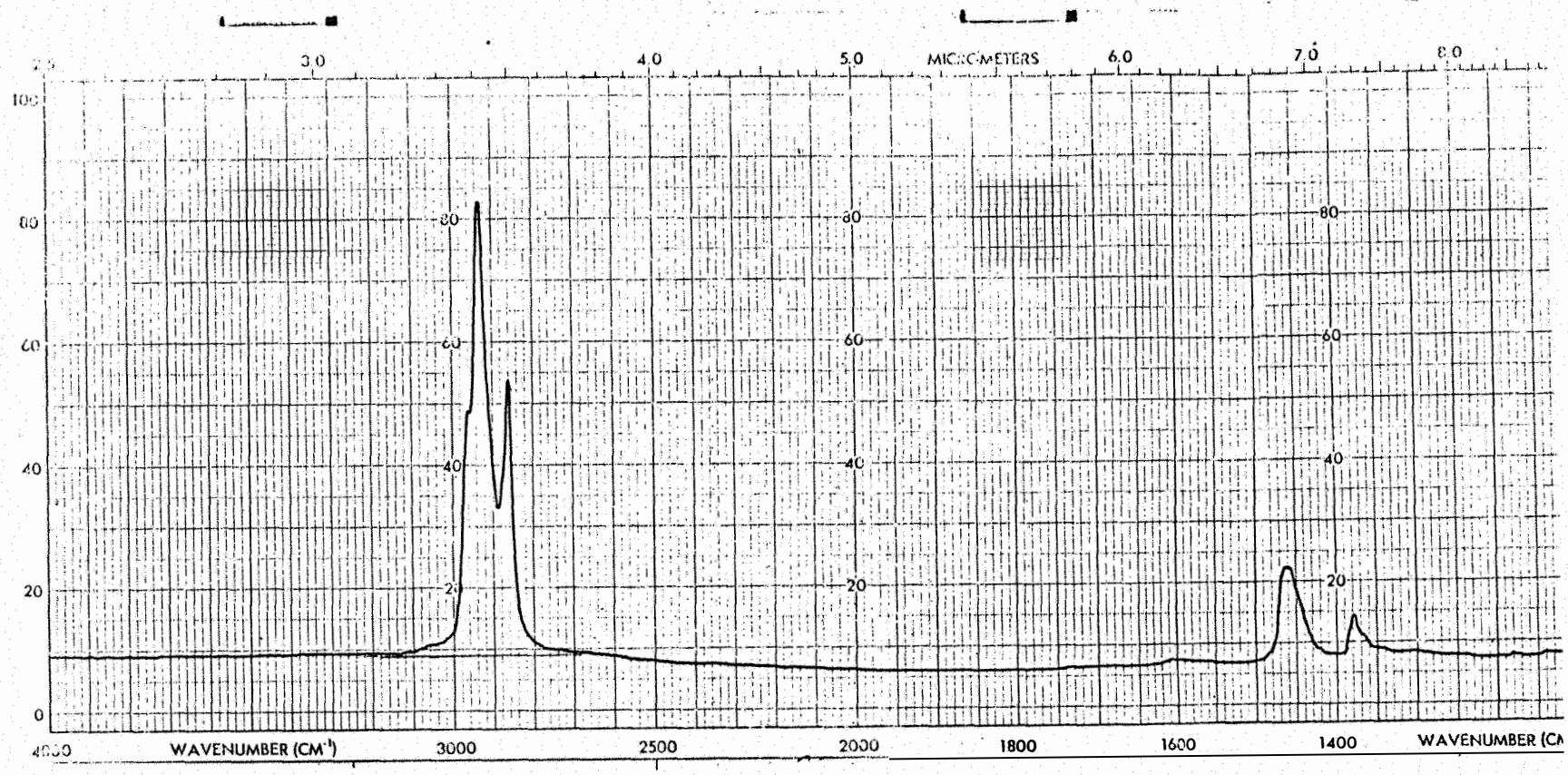


Figure 7: Infrared Spectrum of RA-6 (Absorbance Scale)

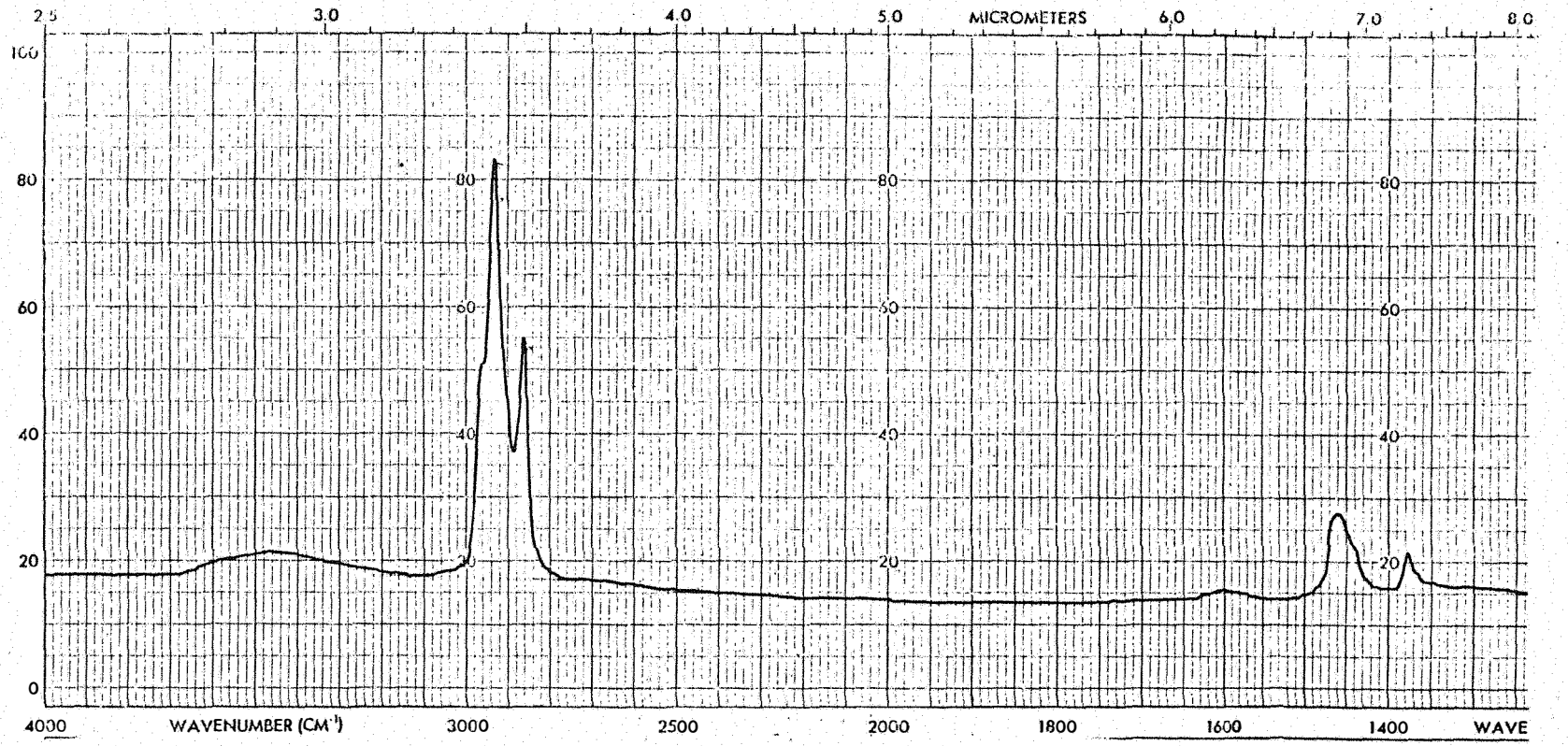


Figure 8: Infrared Spectrum of RA-25 (Absorbance Scale)

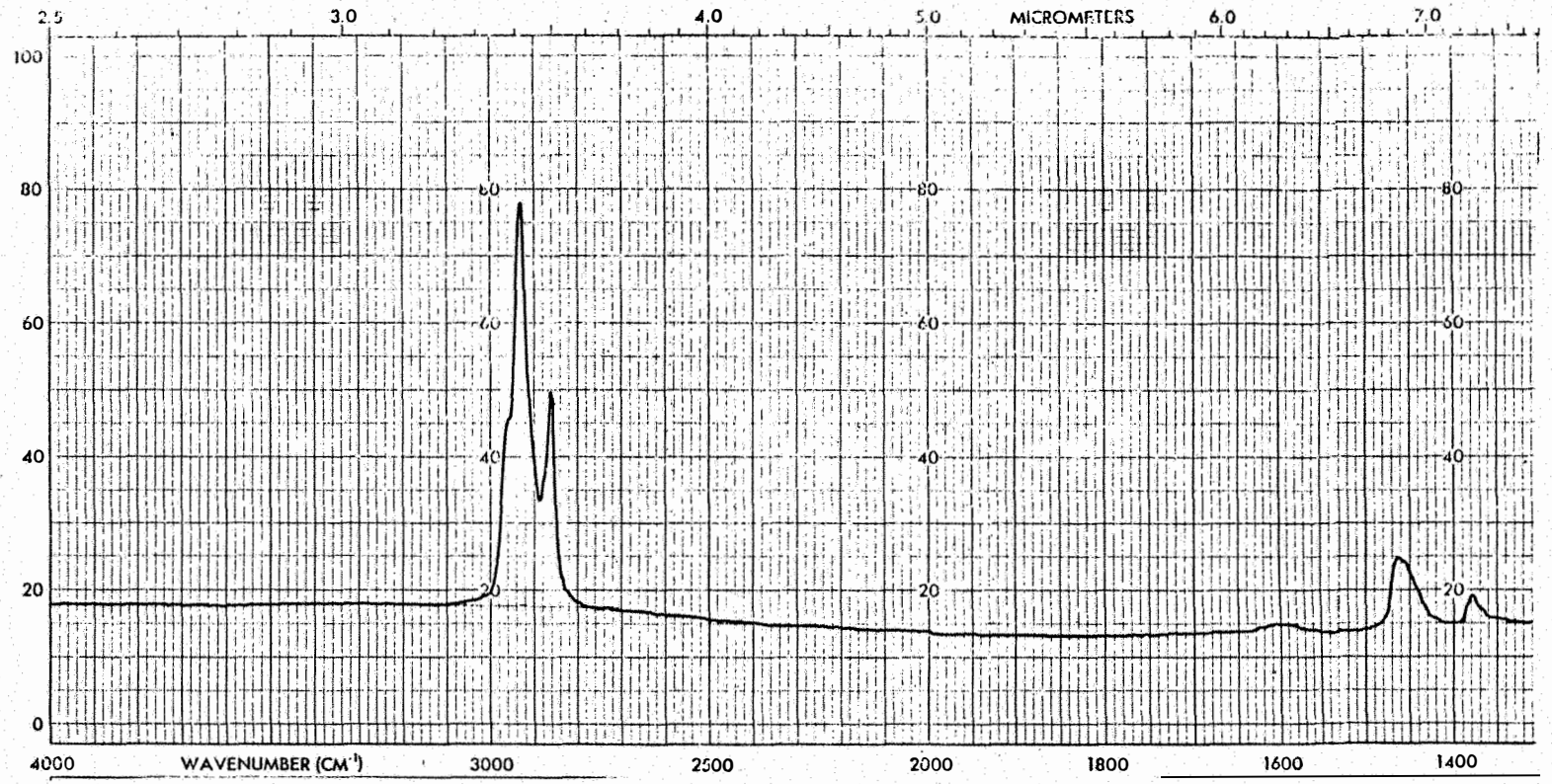


Figure 9: Infrared Spectrum of RA-100 (Absorbance Scale)

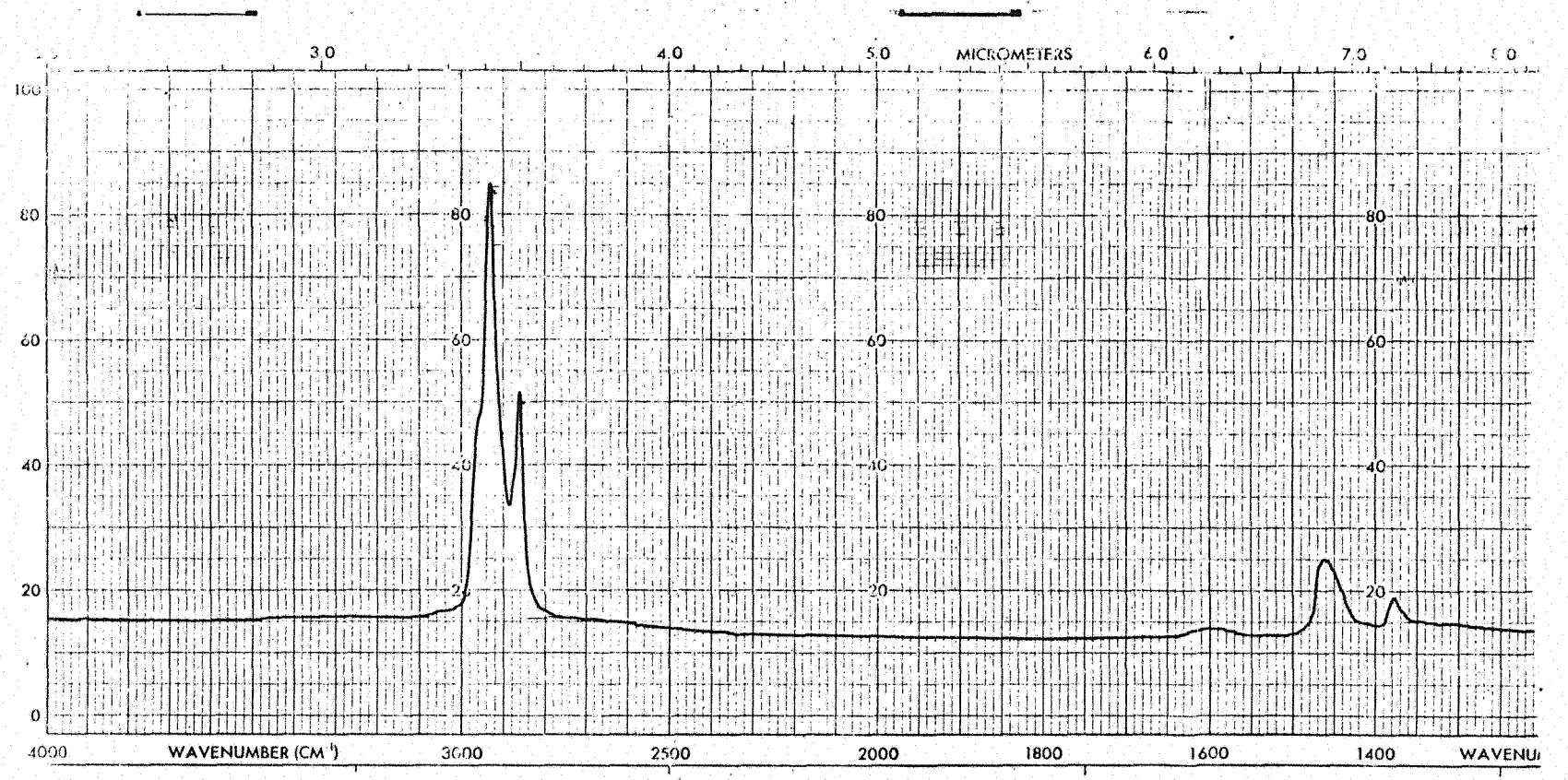


Figure 10: Infrared Spectrum of RA-275 (Absorbance Scale)

The ^{1}H-NMR spectra of the petroleum asphalts are qualitatively similar. The region of stronger resonance between 0.5 and 3 ppm corresponds to hydrogens attached to saturated carbon atoms and the region of weaker resonance between 6.5 and 8 ppm to hydrogens attached to aromatic ring systems. The absence of absorption between these regions rules out the presence of hydrogens attached to carbons of isolated olefinic bonds.[2] The ^{1}H-NMR spectra are shown in Figures 11-15. The centers of absorption for different types of protons are δ = 7.25, H_{ar} aromatic protons; δ = 2.0 - 3.0 H_{α} protons $(-CH_2)_{\alpha}$ to aromatic rings; δ = 1.0 - 2.0, H_{β} protons ($-CH_2-$) and ($-\dot{C}H$); δ = 0.5 - 1.0, H_{γ} protons ($-CH_3$) and saturated methyl protons (Figure 16).[2] Figure 17 presents the data obtained from the ^{1}H-NMR analyses in terms of α, β, γ, and atomatic protons, presented in the form of the H_{α}/H_{γ} and H_{γ}/H_{β} ratios these quantities can be readily determined from the area under the peak by the cut and weigh method.

The "branchiness index" (BI) was defined by Williams in 1958 as the ratio of the heights of ^{1}H-NMR absorption bands due to methyl and methylene groups.[4]

The ^{13}C-NMR spectra (Figures 16 - 20) show a clearly defined pattern characteristic of aliphatic carbon atoms. There are characteristic absorption ranges, $-CH_3$ (14.2 ppm), $-CH_2-$ (23.0 ppm), and $\equiv CH$ (32.1 ppm); however, great overlap between these regions are observed since they are a function of the groups attached to the C atom of interest.[2]

Table 4 relates the relative intensities (and areas) of the major absorptions for AC-3 and the recycling agents. It appears possible to distinguish the recycle agents by the use of these ratios.

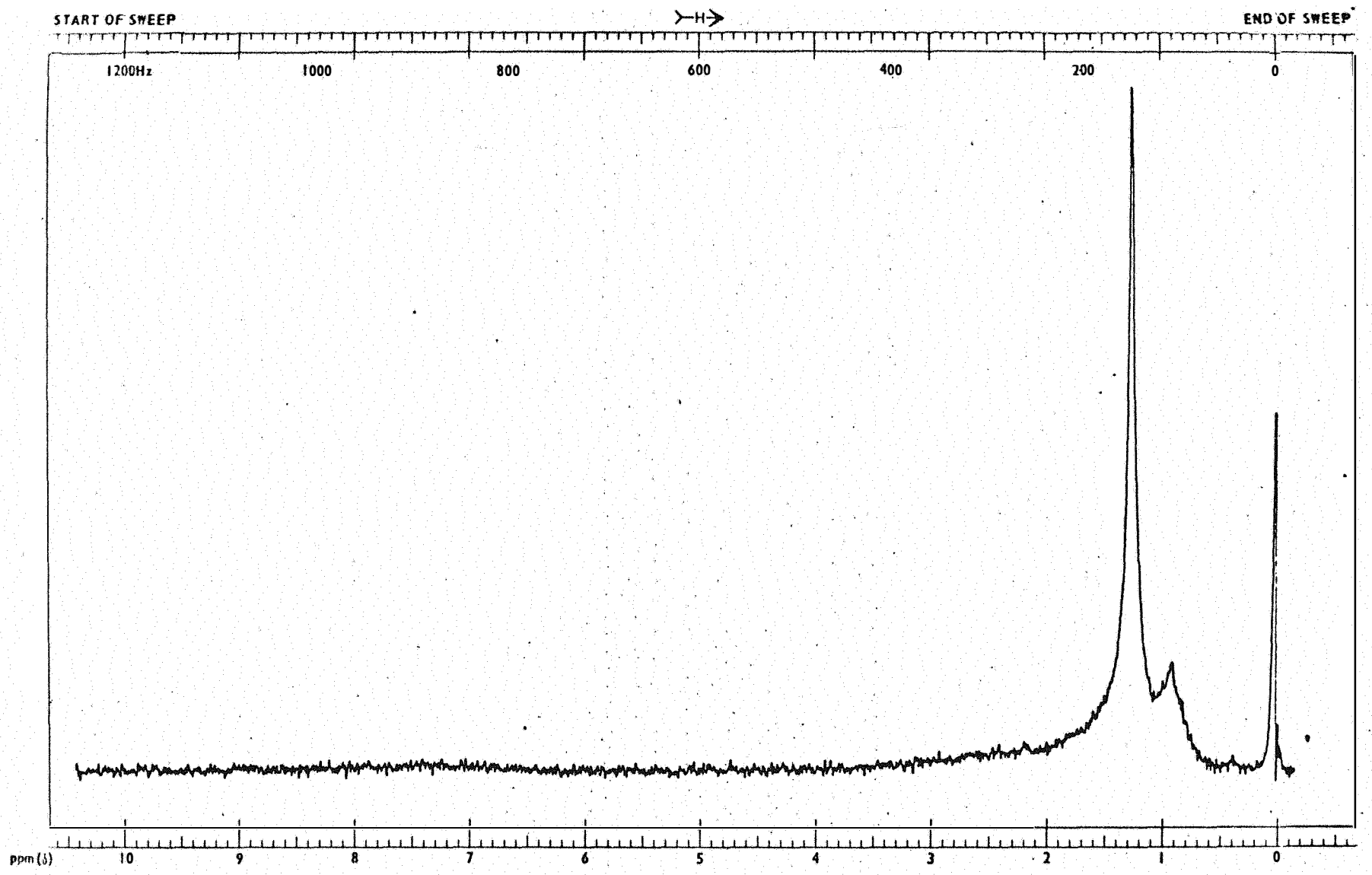


Figure 11: ^{1}H-NMR of AC-3

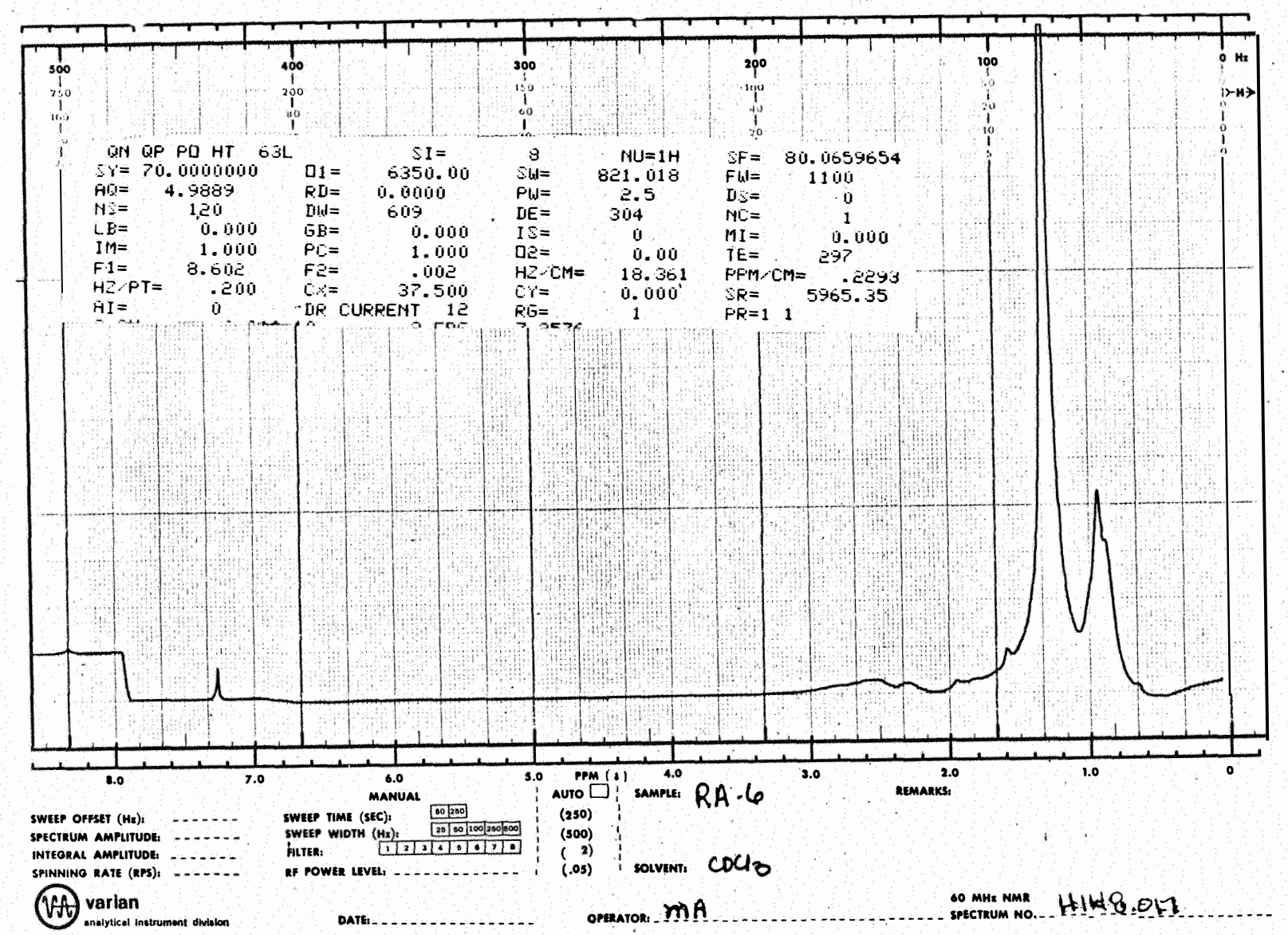


Figure 12: ^{1}H-NMR of RA-6

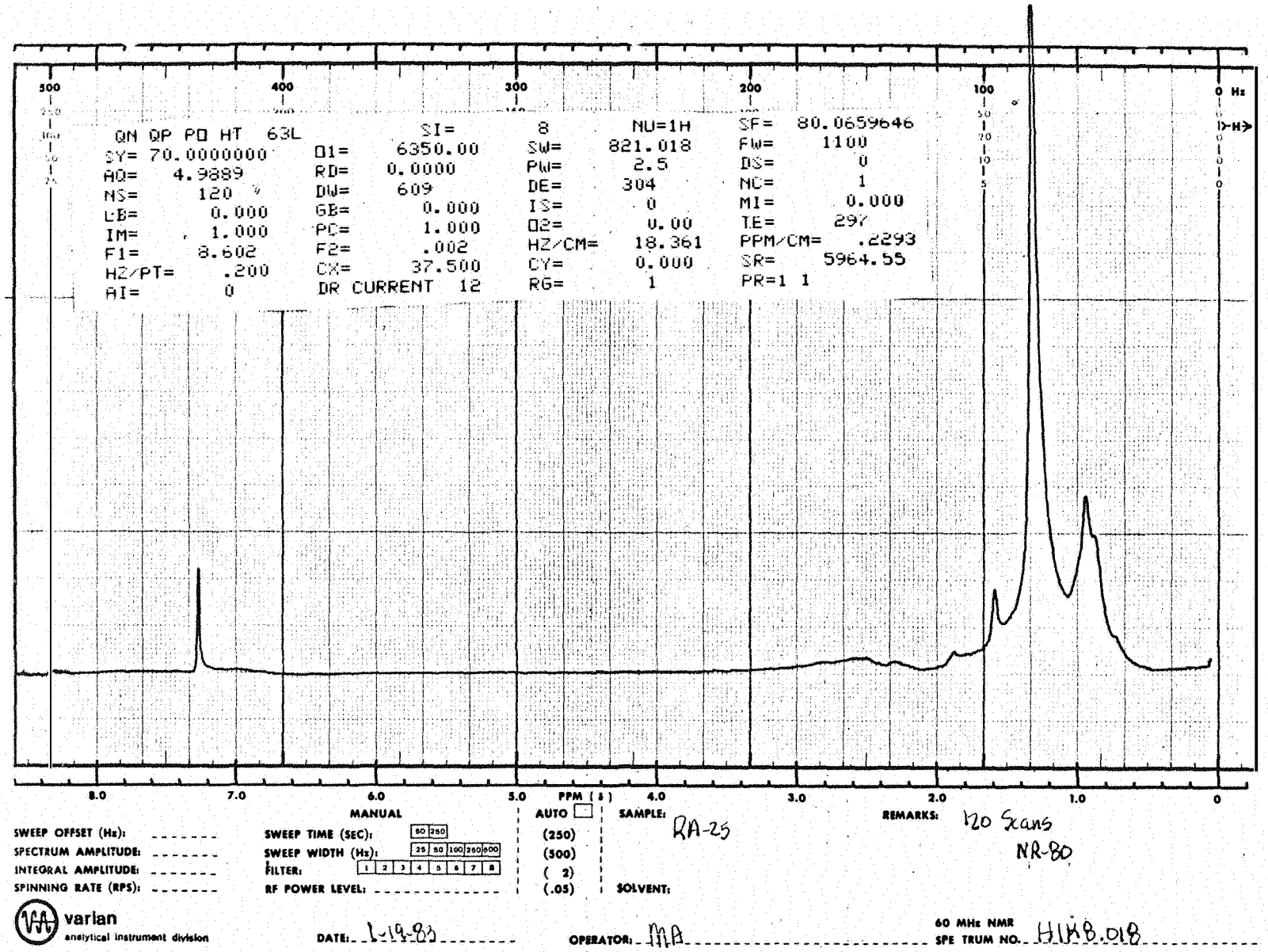


Figure 13: ^{1}H-NMR of RA-25

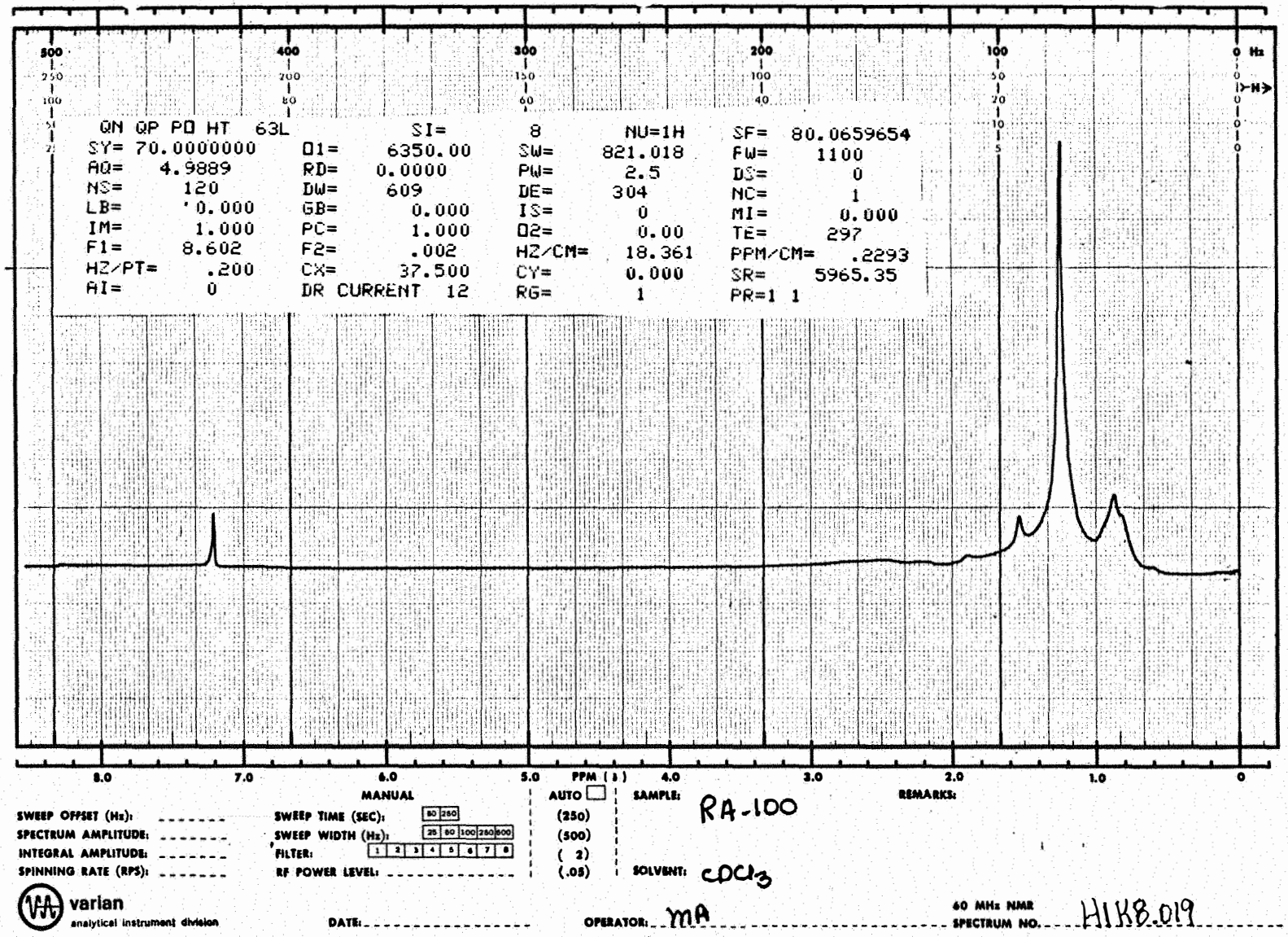


Figure 14: ^{1}H-NMR of RA-100

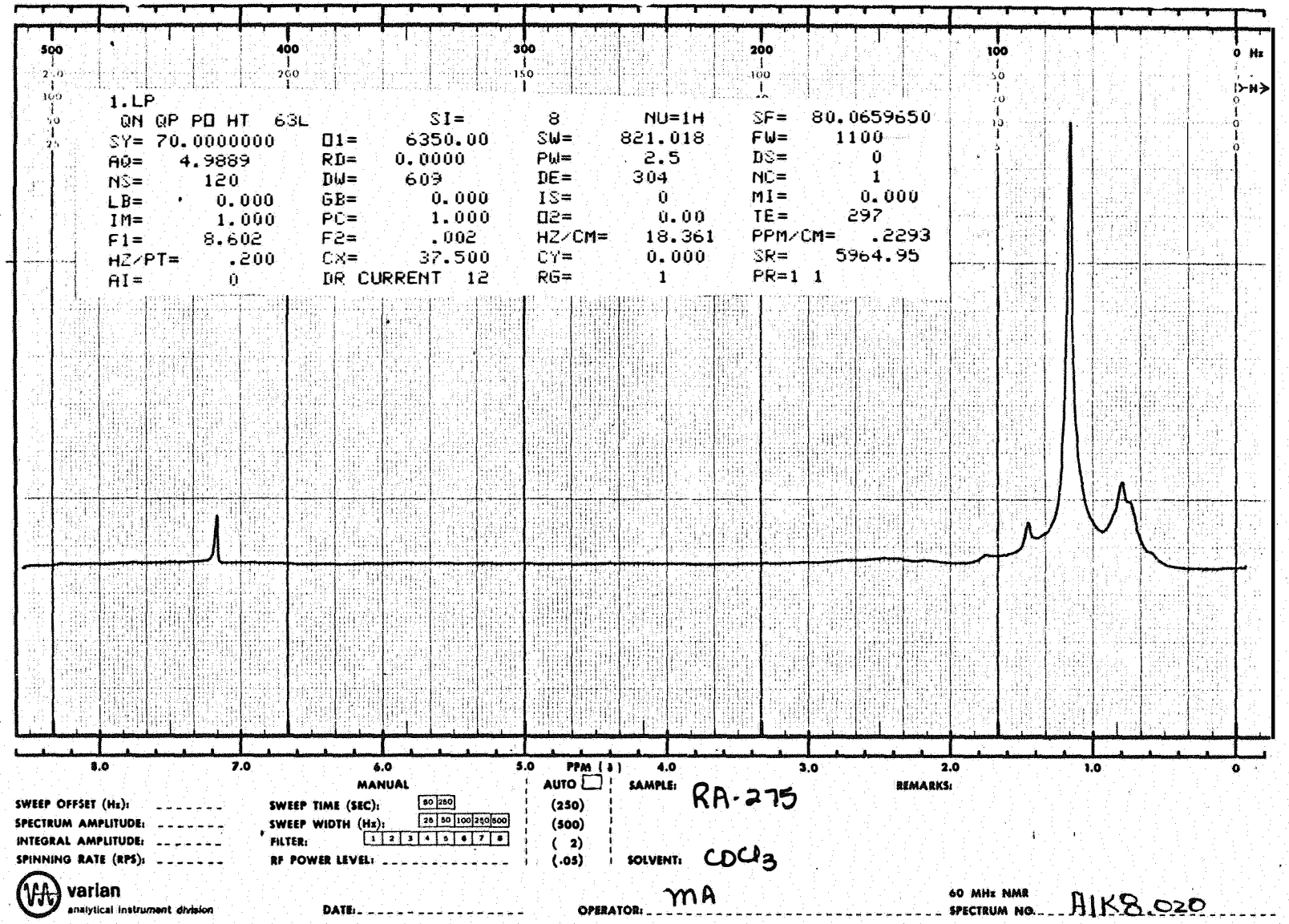


Figure 15: ^{1}H-NMR of RA-275

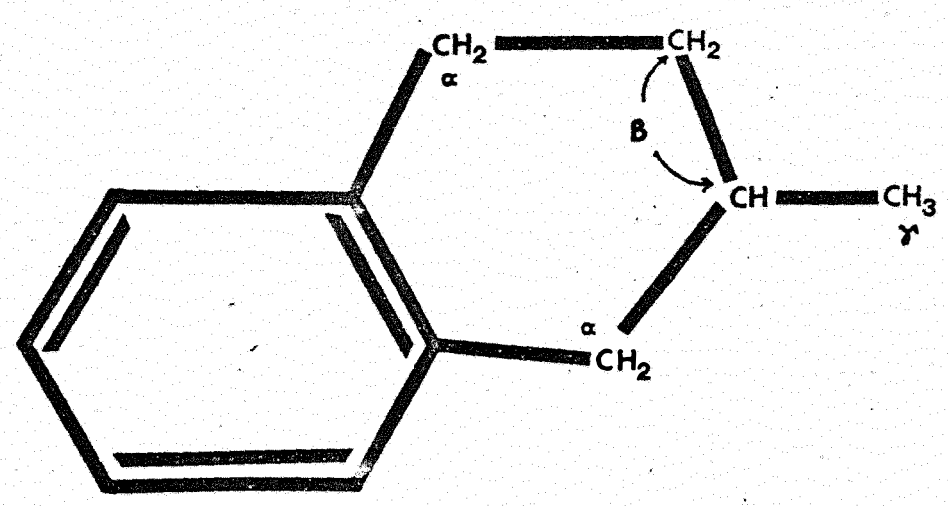
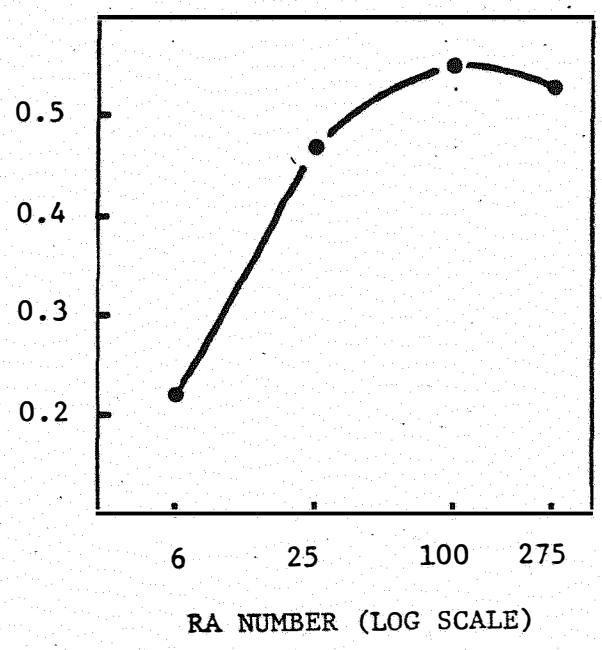


Figure 16: Definition of α, β, and γ positions



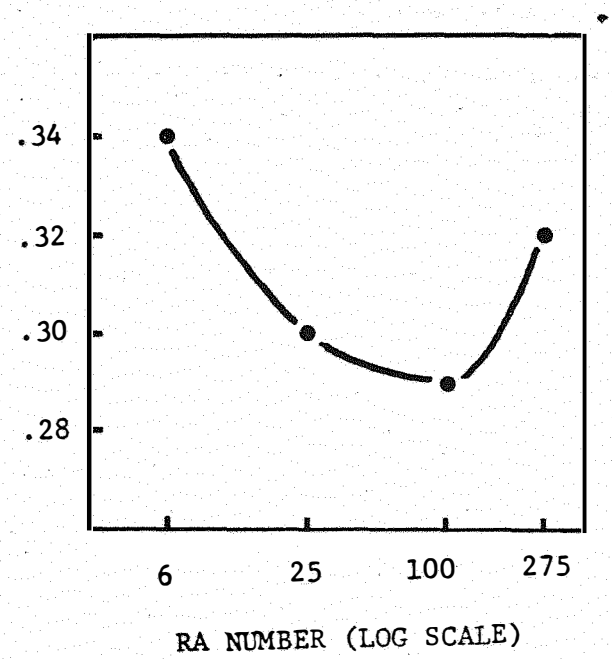


Figure 17: Correlation of ^{1}H-NMR Parameters with Viscosity

Table 3

Correlations of ^{1}H-NMR Parameters with Viscosity

RA Number	H_α/H_γ	BI = H_γ/H_β	Avg. Viscosity cStokes
6	0.22	0.34	600
25	0.47	0.30	2,500
100	0.55	0.29	10,000
275	0.53	0.32	27,500

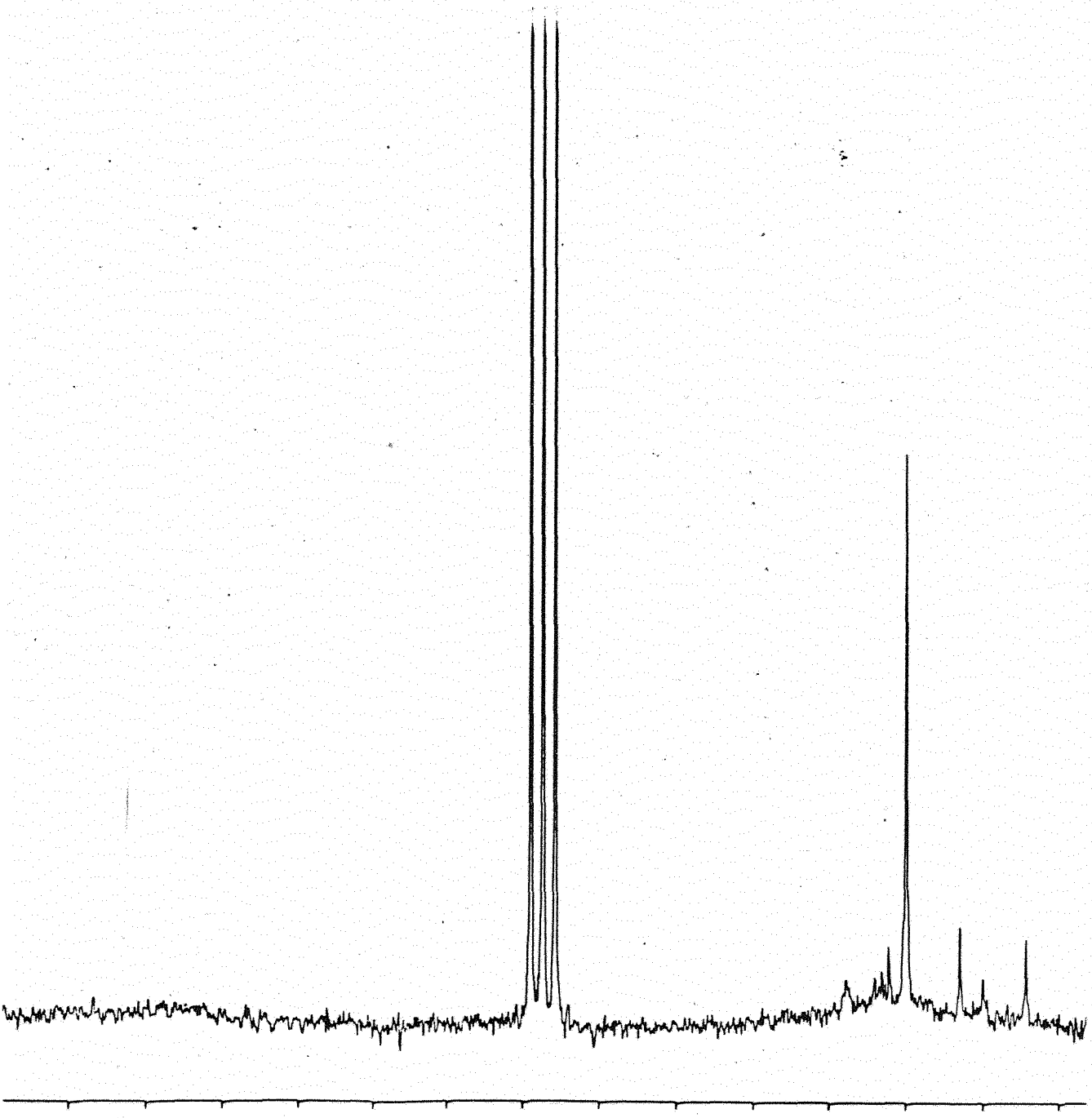


Figure 18: ^{13}C-NMR of AC-3

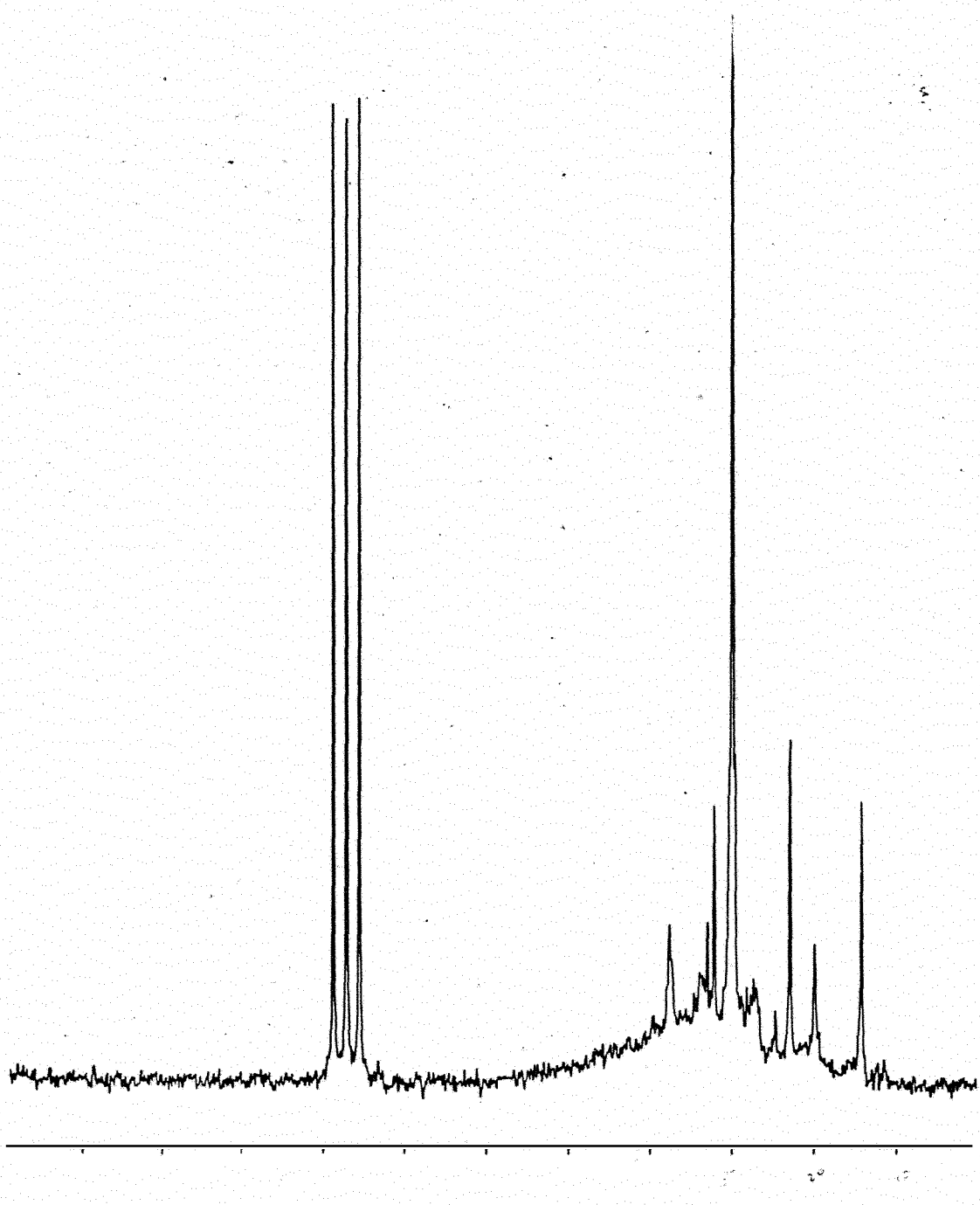


Figure 19: ^{13}C-NMR of RA-6

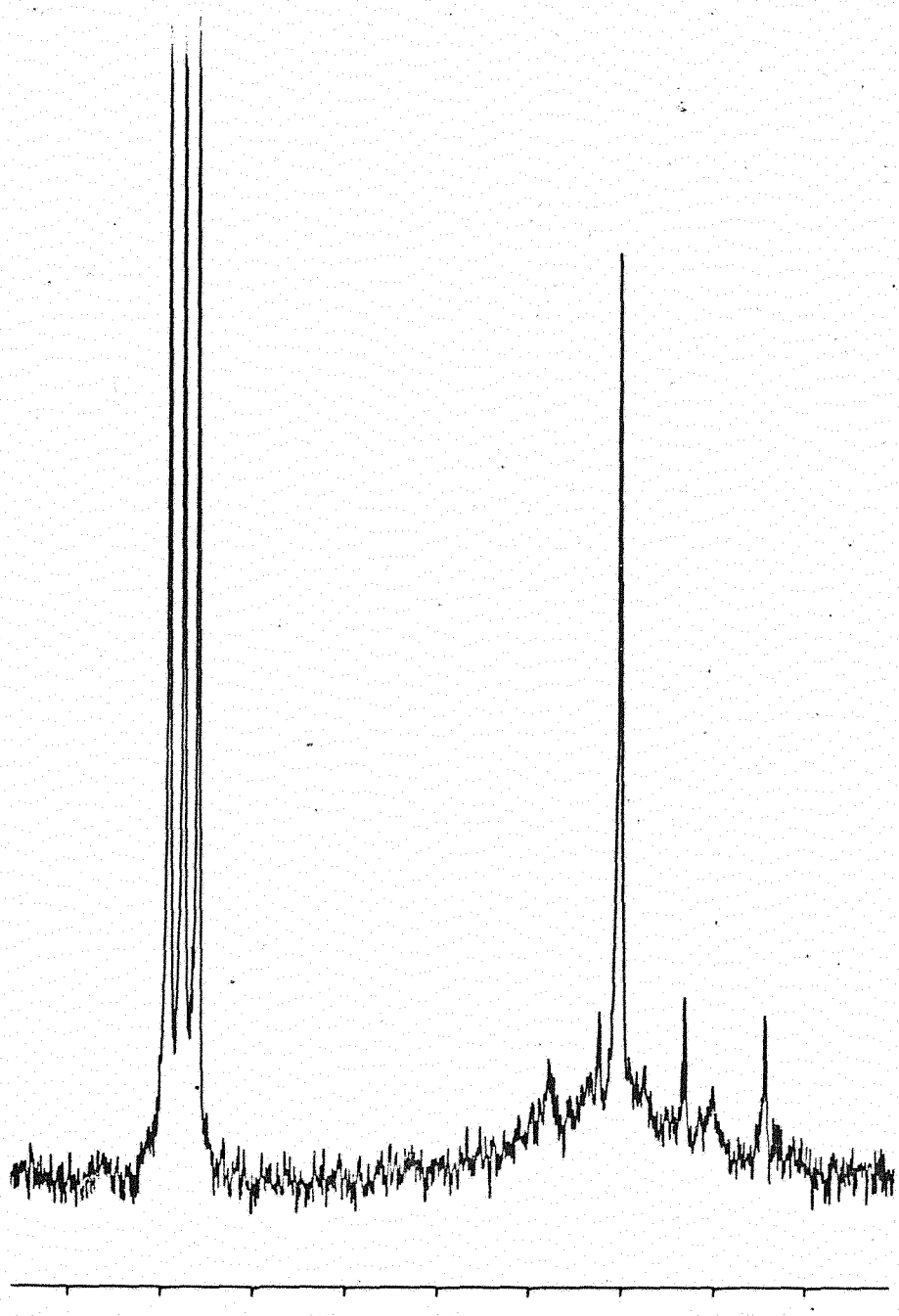


Figure 20: ^{13}C-NMR of AC-25

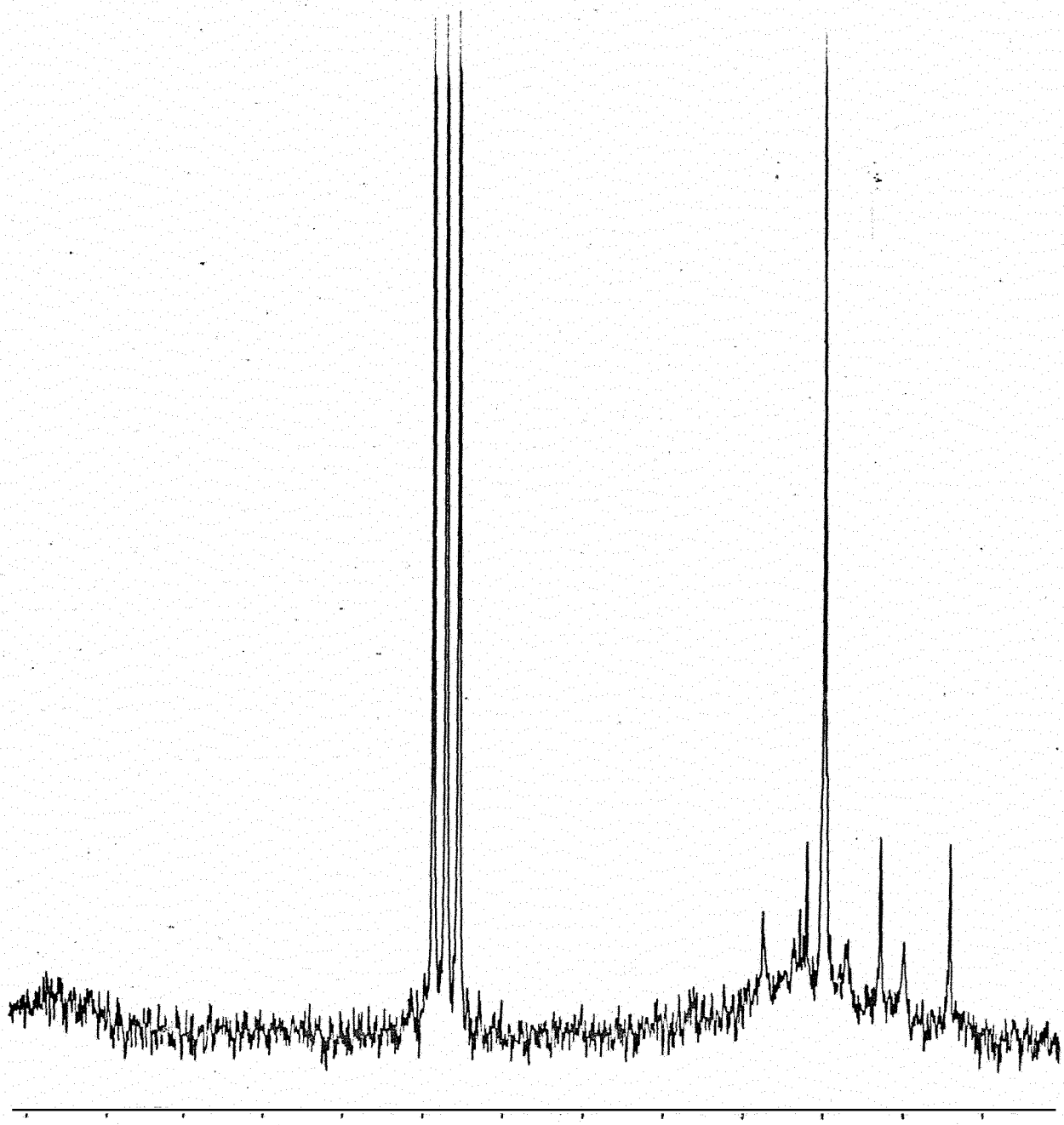


Figure 21: ^{13}C-NMR of RA-100

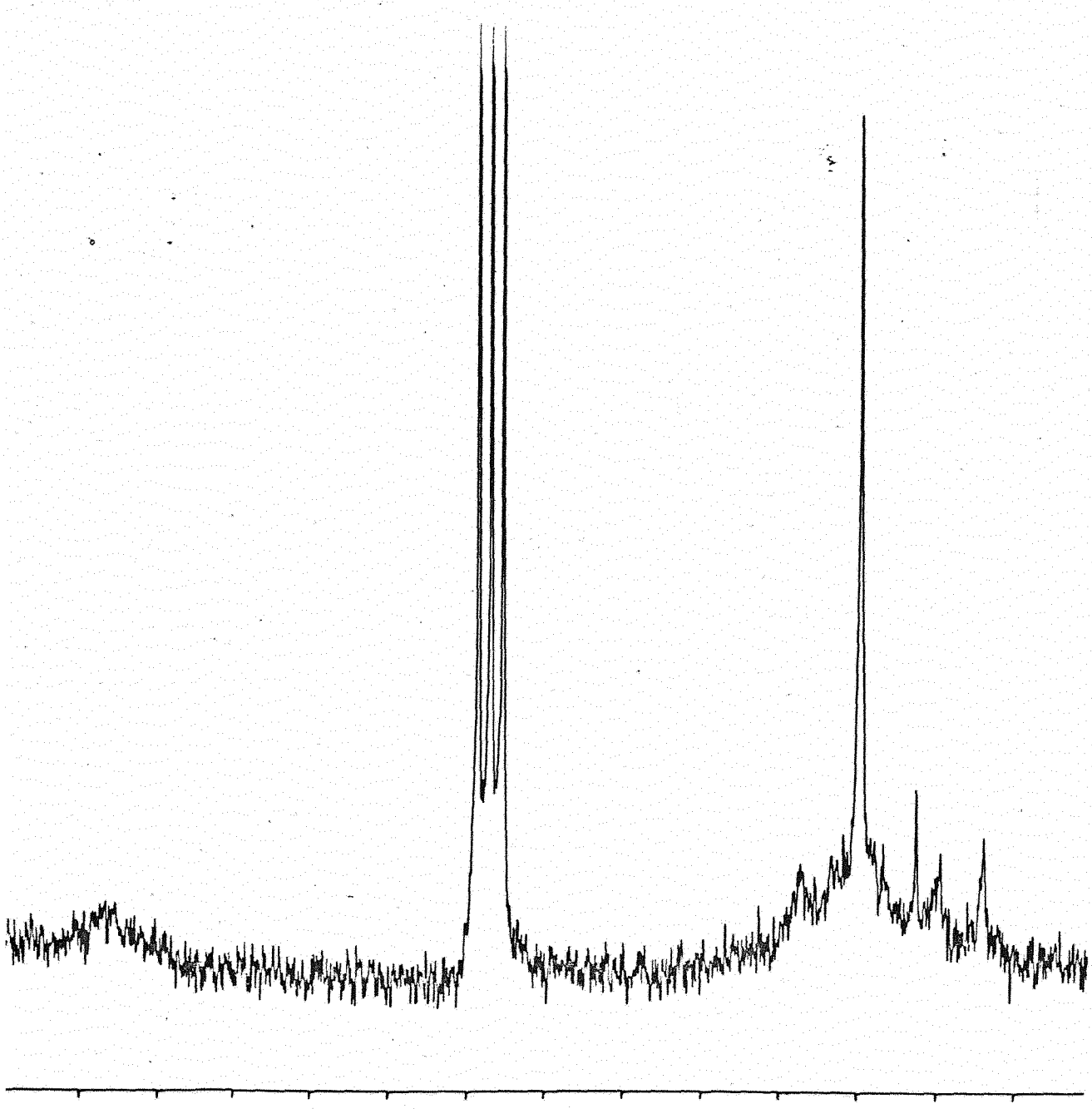


Figure 22: ^{13}C-NMR of RA-275

Table 4

^{13}C-NMR Intensities

Chemical Shift*	14.3	22.9	29.9	32.0
Sample				
AC-3	15.4 (9.9)	17.4 (12.7)	100 (100)	14.0 (11.1)
RA-6	16.1 (13.4)	19.8 (18.7)	100 (100)	15.9 (17.7)
RA-25	17.3 (11.3)	19.2 (10.0)	100 (100)	17.7 (11.7)
RA-100	17.1 (10.6)	17.7 (14.4)	100 (100)	17.2 (18.2)
RA-275	13.8 (8.7)	19.9 (8.8)	100 (100)	16.2 (6.5)

*(ppm downfield from tetramethylsilane)

APPENDIX 1

KANSAS DEPARTMENT OF TRANSPORTATION
SPECIAL PROVISION
TO THE
STANDARD SPECIFICATIONS
EDITION OF 1980

NOTE: Whenever this Special Provision conflicts with the Plans or Standard Specifications, this Special Provision shall govern.

1205 HOT RECYCLING AGENTS

1.0 DESCRIPTION: This specification shall cover the materials to be used as asphalt restorative agents in the Hot Recycling of reclaimed bituminous roadway materials.

2.0 DESIGNATION OF GRADE: The grade of Recycling Agent will be designated on the plans or in the proposal. The Department reserves the right to change grades due to altered quantity or condition of the asphaltic component in the reclaimed materials and/or proportions of reclaimed and new aggregates. When a change of grade is desired by the Department, written notice of such change will be made to the Contractor who shall make the desired change at no additional cost to the Department.

3.0 REQUIREMENTS: Hot Recycling agents shall be the product of specialized refining processes of crude oils, and shall be capable of restorative modification of aged asphalt. They shall conform to the following physical and chemical requirements.

TABLE 1

Property	RA 6	RA 25	RA 100	RA 275
Viscosity, 140°F, cSt	400-800	1000-4000	5000-15,000	20,000-35,000
Flash Point, COC, °F	400 min.	425 min.	450 min.	450 min.
Tests on Residue from TFOT at 325°F:				
Viscosity Ratio (Note 1)	3 max.	3 max.	3 max.	3 max.
Loss on Heating, %	4 max.	3 max.	2 max.	2 max.
Chemical:				
Maltenes Ratio (Note 2)	0.2-1.2	0.2-1.2	0.2-1.2	0.2-1.5
Saturates, wt. %	30 max.	30 max.	30 max.	30 max.

Note 1 Viscosity Ratio = $\frac{\text{TFOT Viscosity @ } 140^{\circ}F}{\text{Original Viscosity @ } 140^{\circ}F}$

Note 2 Maltenes Ratio = $\frac{PC + A_1}{S + A_2}$

Where: PC = Polar Compounds
A_1 = First Acidiffens
A_2 = Second Acidiffens
S = Saturates

4.0 METHODS OF TESTS:

Viscosity, 140°F, cSt	AASHTO T201
Flash Point	AASHTO T48
TFOT	AASHTO T179
Saturates	ASTM D 2006-70
Maltenes Ratio	ASTM D 2006-70

5.0 PREQUALIFICATION OF HOT RECYCLING AGENTS: Manufacturers will be required to submit prequalification samples of any hot recycling agents not previously manufactured by them and/or which have not been used by or on a project of the Department of Transportation for one year. For each hot recycling agent being prequalified or requalified, a one-gallon sample taken from a production batch shall be submitted, along with a copy of the manufacturer's results on the sample, to the Engineer of Tests.

Any change in formulation will necessitate requalification.

6.0. BASIS OF ACCEPTANCE: Section 1203 of Standard Specifications

#	CURSOR	FREQ	PPM	INTEGRAL	INTENSITY
1	3962	1585.049	78.8190	26.687	28.444
2	4005	1553.156	77.2330	27.362	28.804
3	4043	1521.143	75.6411	25.898	27.877
4	5239	645.848	32.1158	2.076	1.658
5	5300	601.048	29.8880	18.810	11.835
6	5492	459.763	22.8624	2.381	2.063
7	5727	287.013	14.2721	1.862	1.823

1. AC-3

#	CURSOR	FREQ	PPM	INTEGRAL	INTENSITY
1	3961	1581.887	78.6617	8.114	19.219
2	4005	1549.875	77.0698	8.435	18.929
3	4048	1517.994	75.4845	7.895	19.343
4	5088	753.524	37.4701	3.365	2.937
5	5215	659.914	32.8152	1.806	3.000
6	5238	643.088	31.9785	3.858	5.238
7	5299	598.331	29.7529	21.798	33.010
8	5308	591.680	29.4222	2.839	6.265
9	5491	456.949	22.7225	4.077	6.532
10	5726	284.171	14.1308	2.916	5.315

2. RA-6

#	CURSOR	FREQ	PPM	INTEGRAL	INTENSITY
1	3934	1607.012	79.9111	1.672	2.058
2	3951	1586.888	78.9104	38.654	22.237
3	3972	1579.218	78.5290	2.264	2.850
4	4005	1554.965	77.3230	44.682	22.948
5	4024	1540.684	76.6128	2.573	3.112
6	4031	1535.546	76.3573	2.712	3.895
7	4048	1523.052	75.7361	33.420	21.946
8	5090	757.145	37.6502	2.743	2.017
9	5239	647.618	32.2038	4.983	2.832
10	5267	626.472	31.1523	3.654	2.196
11	5300	602.753	29.9728	42.527	15.371
12	5326	583.248	29.0029	2.113	2.055
13	5492	461.550	22.9513	4.245	3.055
14	5726	288.899	14.3659	4.822	2.768

3. RA-25

#	CURSOR	FREQ	PPM	INTEGRAL	INTENSITY
1	3961	1581.717	78.6533	21.108	37.662
2	4005	1549.725	77.0624	20.584	40.060
3	4048	1517.844	75.4771	19.613	37.847
4	5090	752.085	37.3991	4.001	2.436
5	5215	659.630	32.8011	1.994	2.567
6	5239	642.476	31.9481	3.352	3.899
7	5299	597.709	29.7220	18.837	22.609
8	5491	456.593	22.7048	2.644	4.002
9	5727	283.522	14.0986	1.954	3.864

4. RA-100

#	CURSOR	FREQ	PPM	INTEGRAL	INTENSITY
1	3930	1603.341	79.7286	3.282	2.429
2	3961	1580.186	78.5771	45.591	22.154
3	3974	1570.667	78.1038	2.546	3.592
4	4005	1548.220	76.9876	46.742	22.862
5	4023	1534.794	76.3200	3.891	3.339
6	4048	1516.294	75.4000	38.376	21.241
7	5087	752.616	37.4250	1.735	2.086
8	5194	673.770	33.5042	4.179	2.250
9	5214	658.950	32.7673	5.073	2.168
10	5238	641.282	31.8887	3.309	2.739
11	5248	633.931	31.5232	2.146	2.228
12	5253	630.692	31.3621	1.891	2.345
13	5259	626.006	31.1291	1.852	2.136
14	5268	619.113	30.7863	4.740	3.154
15	5300	596.121	29.6430	47.732	16.916
16	5315	584.561	29.0682	1.352	2.407
17	5320	581.194	28.9007	1.158	2.055
18	5333	571.623	28.4248	3.809	2.171
19	5346	562.006	27.9466	4.859	2.133
20	5378	538.664	26.7859	2.731	2.143
21	5491	455.214	22.6362	4.219	3.361
22	5573	394.879	19.6360	3.159	2.018
23	5726	282.397	14.0426	4.161	2.344

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References

1. R.L. Hubbard and E.K. Stanfield, "Determination of Asphaltenes, Oils, and Resins in Asphalt," Anal. Chem., 20, 460 (1948).

2. R.M. Silverstein, G.C. Bassler, and T.C. Morrill, Systematic Identification of Organic Compounds," 4th ed., John Wiley, N.Y. (1981).

3. R.B. Williams, "Characterization of Hydrocarbons in Petroleum by Nuclear Magnetic Resonance Spectrometry," Am. Soc. Testing Mater. Spec. Tech. Publ. No. 224, 168 (1958).