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NMR Analysis of Mixed Pentaerythritol, Dipentaerythritol, and 1, 1, 1-Trimethylolpropane Esters

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ABSTRACT

Benzene solutions of mixed pentaerythritol, dipentaerythritol, and 1,1,1-trimethylolpropane esters may be quantitatively assayed by proton NMR spectroscopy with an absolute accuracy of ± 5 mole-% for each of the ester types. Higher accuracies are possible if a calibration curve is used. Average acid chain length and the approximate degree of chain branching are also obtained.

The NMR method can be used for monitoring base stocks, checking blend compositions, and determining constancy of formulation of oils qualified under specification MIL-L-23699. NMR analyses of a group of commercial esters and of several aircraft engine lubricant formulations have been made. Results were obtained on both the Varian A-60 and HA-100 spectrometers, with comparable accuracy. The A-60 is felt to be the preferred instrument, however, because its integrals are simpler to process.

PROBLEM STATUS

This is a final report on this phase of the problem; work on other phases of the problem is continuing.

AUTHORIZATION

NRL Problem C07-04
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NMR ANALYSIS OF MIXED PENTAERYTHRITOL,
DIPENTAERYTHRITOL AND
1,1,1-TRIMETHYLOLPROPANE ESTERS

INTRODUCTION

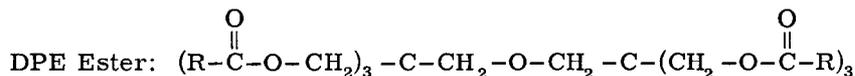
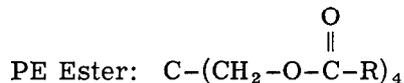
Neopentyl Type Esters

Suitable lubricating oils for high-performance jet aircraft engines are increasingly difficult to obtain as engine design advances. Mineral oils were satisfactory lubricants for the early jet engines with oil-out temperatures at the bearings of 210° to 260° F, while it was necessary to employ aliphatic diester oils for the engines of the early 1950's (340° to 400° F oil-out temperatures). The 600° to 650° F oil-out temperatures of the newer jet engines such as the J-58 and J-93 severely curtail the useful life of diester oils. Their high-temperature viscosity is low, resulting in marginal lubricating properties. Gear load additives do not improve lubricity sufficiently.

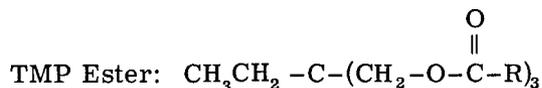
The low-temperature viscosity requirement contained in specification MIL-L-23699 (1) has allowed the qualification of neopentyl type ester oils. The greater viscosity of these oils at high temperature, along with their increased oxidation resistance and thermal stability relative to the aliphatic diesters, appear to satisfy current requirements. The benefits gained in the substitution of neopentyl type ester oils for the aliphatic diesters include cleaner engine operation, longer periods between engine overhauls, longer useful lubricant life, and better load-carrying capacity. The neopentyl type esters should not be regarded as the ultimate, however, since the production of more powerful engines will require the development of lubricating oils of higher oxidative and thermal stabilities.

The qualification tests to which lubricants may be subjected are time consuming and expensive. It is therefore important to determine if the makeup of a once-qualified lubricant product varies significantly in production batches. It is likely that various blends which may meet the viscosity and other physical requirements will show differing susceptibilities to degradation; it would be desirable to monitor composition in order to detect constituents which are found to degrade performance.

Most of the lubricant formulations which have been submitted for qualification under MIL-L-23699 are blends of mixed pentaerythritol (PE) esters and mixed dipentaerythritol (DPE) esters; the acid chains are in the C₅ to C₉ range:



Some oils also contain mixed 1,1,1-trimethylolpropane (TMP) esters:



Also present, primarily to improve oxidation stability and minimize gear wear, are varied additive packages.

Analytical procedures are available for the determination of PE or DPE in mixtures (2-7). A method for analyzing the mixed esters might involve saponification, followed by analysis of the alcohols for PE or DPE. Any such chemical method is laborious and would be complicated by the necessity for determining TMP content as well.

A rapid, nondestructive method for quantitative analysis of mixed PE, DPE, and TMP esters by means of proton NMR spectroscopy is presented here.

The NMR Method

Nuclear magnetic resonance (NMR) is a form of spectroscopy based upon the spin energy levels of nuclei which possess magnetic moments and associated nuclear spins. The separation of the nuclear spin energy levels is proportional to the magnitude of an externally applied dc magnetic field. Irradiation with energy (usually in the radio-frequency range) corresponding to the separation of adjacent energy levels causes nuclear spin transitions which are detectable with a suitable apparatus. The resulting spectra give detailed information about molecular structures.

In this study, proton (H^1) NMR was employed. Qualitative analysis is possible because each chemically different type of proton gives rise to a signal at a distinct spectral location. Quantitative analyses may be made because the intensity of each signal is proportional to the number of nuclei in the sample which are resonant at that frequency; simple graphical or electronic measurement of the area under each signal is all that is necessary. At least one line or group of lines must be assignable to a known molecular grouping to provide a calibration.

EXPERIMENTAL PROCEDURE

Samples

The samples of pentaerythritol tetracaproate (PETC) and dipentaerythritol hexacaproate (DPEHC) were prepared at NRL.* Samples NRL-S-300, NRL-S-304, and NRL-S-302 are commercially available mixed pentaerythritol and/or dipentaerythritol esters. The sample designated NRL-T is a commercially available TMP ester base stock. The remaining oils were test samples submitted by the manufacturers.

Standard reagent grade, thiophene-free benzene was used as the solvent.

PE-DPE standard samples were made by mixing weighed amount of PETC and DPEHC. An analytical balance was used and weights were determined to ± 0.1 mg. The mixtures were taken up in benzene to give 20 vol-% solutions. NMR samples of the commercial esters or lubricant formulations were made by diluting 0.15 ml of each with 0.6 ml of benzene. All additives remained in solution and did not interfere with the NMR measurements.

NMR Measurements

The NMR spectra were recorded and calibrated with a Varian HA-100 spectrometer in the field-sweep mode, with the field locked on the solvent benzene peak. One percent

*These samples were synthesized by P. Sniegowski and J.G. O'Rear of the Synthetic Oils Section, Surface Chemistry Branch.

of tetramethylsilane (TMS) served as the internal reference and all peak positions are reported in ppm downfield from TMS.

The PE-DPE-TMP portion of each sample was integrated at least five times using maximum full-scale pen deflection for more accurate integral counts. The integration of the entire spectrum, used in the calculation of average acid chain length and methyl count, was carried out a minimum of three times. Solvent blanks were run and appropriate corrections made.

The A-60 spectra and integrals were determined in a similar fashion, but 60 Mc peak calibrations were not made.

The A-60 integrals showed flat plateaus before and after the signals of interest (Fig. 1); integral calculations were thus straightforward. The HA-100 integrals, however, even after optimum adjustments of phase and detector zero showed a spurious upward drift through the DPE region (Fig. 2). This apparently is associated with fourth-order magnetic field gradients which cannot be eliminated completely by the field shims. Using standardized spectrometer settings, this effect was corrected for by taking the PETC results as a blank in the region from 3.0 to 3.7 ppm. An additional complication of the 100-Mc spectrum is the near superposition of the DPE signal and the upfield C^{13} satellites of the PE and TMP peaks ($J_{C^{13}H} \approx 150$ cps). The added intensity can cause an appreciable error in the calculated DPE content at low concentrations. In the 100 Mc integrals, 0.55% of the PE and TMP integrals (1/2 of the C^{13} natural abundance) was subtracted from the DPE integral, in addition to the blank correction. At 60 Mc the PE and TMP C^{13} satellites fall well away from the DPE, and no correction is needed. The low-field C^{13} satellites of the acid α -CH₂ protons fall in the DPE region at 60 Mc but are apparently quite diffuse. If close cutoffs are taken for the DPE integral, this error can be minimized.

The results obtainable with the A-60 are comparable in absolute accuracy with those of the HA-100; the statistical scatter in a series of measurements is smaller than the estimated absolute error in spite of the lower sensitivity of the A-60. Considering that the A-60 is by far the most common NMR spectrometer and that its integrals are easier to process, it is felt that it would be preferred to the HA-100 for routine quantitative determinations of PE-DPE-TMP mixed ester content.

The absolute accuracy of the determinations could be improved by running a calibration curve on mixtures of known composition; accuracies of ± 2 mole-% would probably be possible.

DISCUSSION

Spectral Analysis

The 100 Mc proton NMR spectra of PETC and DPEHC are shown in Fig. 3. The peak assignments are straightforward (Table 1). The fine structure appearing in the acid proton region (*c-f*) is due to spin-spin coupling among chemically different nuclei; it is not of interest for the present purposes.

Because of the large chemical shift between the alcoholic methylene groups of PETC and DPEHC (*a*) and the ethereal methylene groups of DPEHC (*b*), quantitative assay of the PE-to-DPE ratio in mixtures of the esters is easily carried out.

Additional quantitative information can be obtained by integrating the signals from the acid chains (*c-f*), and methyl groups (*f*). Since there is one acid group for each alcoholic methylene group (*a*), the integrated intensity of (*c-f*), designated I_{c-f} , can be

Table 1
Peak Assignments of the Proton NMR Spectra of Pentaerythritol
Tetracaproate (PETC) and Dipentaerythritol Hexacaproate (DPEHC)

Peak* Designation	Position† (ppm)		Assignment
	PETC	DPEHC	
<i>a</i>	4.21	4.20	Alcohol methylene
<i>b</i>	-	3.35	Ether methylene
<i>c</i>	2.11	2.15	Acid α -methylene
<i>d</i>	1.52	1.55	Acid β -methylene
<i>e</i>	1.17	1.19	Acid γ - and δ -methylene
<i>f</i>	0.83	0.84	Acid methyl

*See Fig. 3.

†Peak positions (or multiplet centers) are given in ppm downfield from internal TMS and are accurate to ± 0.01 ppm.

converted to an average acid chain length. Similarly, the integrated intensity of the methyl group, I_f , is indicative of the degree of chain branching.

Figure 4 shows the spectrum of a TMP-ester mixture. The signal due to the alcoholic methylene proton (a') at 4.10 ppm is shifted upfield slightly compared to the a signal of the PE and DPE esters. Fortunately, the shift between the a and a' signals in mixtures of TMP and PE-DPE esters is large enough to allow a fairly good determination of the individual a and a' integrated intensities. Since some of the proprietary oils contain TMP esters, it is important to be able to analyze for them in the presence of PE/DPE esters. The choice of solvent bears on this matter, as discussed in the next section.

Solvent

The NMR spectra of the undiluted esters are poorly resolved (Fig. 5a), probably because of viscosity effects. The samples of Fig. 5 contain equal parts by volume of NRL-S-300, NRL-S-302, and NRL-T.

While the usual NMR solvents, CCl_4 and CDCl_3 , increase peak separation and improve resolution (Figs. 5b and 5c, respectively), the greatest separation of the a signals from the a' signal occurs with benzene (Fig. 5d). The solvent effects which usually eliminate benzene as the solvent of choice work to advantage in this case, the reduced overlap of the PE-TMP signals resulting in more accurate quantitative measurements.

QUANTITATIVE ASPECTS

Ester Content

A consideration of the commercial oils shows that there are three pieces of information desired - %PE, %DPE, and %TMP - and that there are three measurable parameters - I_a , $I_{a'}$, and I_b .

It is noteworthy that if tripentaerythritol (TPE) esters are present in more than trace amounts it will not be possible to obtain a correct analysis, for the *a* and *b* signals of TPE esters fall under the *a* and *b* signals of PE and DPE esters. Fortunately, TPE constitutes only a small percentage of commercial PE (7) and is not expected to be present to any significant extent in the commercial ester mixtures. It has been detected during this study only in the pot residue from a fractional distillation of NRL-S-302.

The analysis for PE, DPE, and TMP is based on the parameters listed in Table 2.

The two simultaneous equations arising from the PE and DPE signal intensities are easily solved to yield the following equation:

$$\text{moles PE/moles DPE} = \frac{I_a - 3I_b}{2I_b} \quad (1)$$

In a sample also containing TMP esters, the following relationship results:

$$\text{moles TMP: moles DPE: moles PE} = I_{a'}/3 : I_b/2 : (I_a - 3I_b)/4 \quad (2)$$

Table 2
The Number of Protons of Type *a*, *a'*, and *b* Contained in Each Molecule of a PE, DPE, or TMP Ester

Ester	Number of Protons/Molecule of Type		
	<i>a</i>	<i>a'</i>	<i>b</i>
PE	8	0	0
DPE	12	0	4
TMP	0	6	0

Average Acid Chain Length and Chain Branching

The relationship between the number of protons (N_H) and the number of carbon atoms (N_C) in the chain fragment of a saturated aliphatic carboxylic acid is given by the equation

$$N_H = 2N_C - 1 \quad (3)$$

Hence, the integrated intensity of the signals from the protons of the acid chains (*c-f*) can be converted to an average acid chain length. The integrated intensity of *a* (and *a'*, if present) provides the calibration, since there is one acid chain for each *a* or *a'* methylene group.

Equation (3) holds for branched chains, but not for cyclics or unsaturates. The last two classes have not been detected in the esters studied.

The presence of TMP esters complicates the calculation because the signals from the ethyl portion of the TMP fragment fall in the (*c-f*) region, giving anomalously large integrals for the acid chains. This can be corrected for rigorously by subtracting from I_{c-f} an amount equal to the contribution of the five ethyl protons of the TMP molecules, or $5/6 I_{a'}$.

The separation of the methyl group signals (*f*) from the remainder of the acid signals allows a rough calculation of the amount of chain branching. For normal-paraffin chains,

I_f should be $1.5(I_a + I_{a'})$. Chain branching will increase the relative intensity of f . Because the f protons are not completely separated from the e protons and because chain branching tends to shift the methyl signals to lower field, the methyl group count here should be regarded as only approximate.

The signals at 0.99 and 1.06 ppm in Fig. 6b are attributed to some isopropyl fragments and illustrate the low-field shift mentioned above.

If TMP esters are present, I_f must be decreased by $I_a/2$ to correct for the methyl group contribution of the TMP fragment.

Calibration with Standard Samples

In order to determine the absolute accuracy of the NMR method for measuring PE-DPE content of mixed esters, a series of standard samples of known composition was made up from highly purified PETC and DPEHC which were synthesized at NRL.

Listed in Table 3 are the known compositions of the standard samples and the compositions determined by NMR analysis in benzene solution. The results were obtained on two different instruments, and HA-100 research spectrometer and an A-60 analytical spectrometer, which is common in large laboratories. The error stated is the standard deviation of the measurement; it is not indicative of absolute error in PE content.

The analyses compare well between the two instruments, but both give high PE contents due to an undetermined systematic error. It appears reasonable to claim a ± 5 mole-% absolute accuracy for PE content as determined by the NMR method, based upon these results.

Table 3
A-60 and HA-100 NMR Analyses of PETC-DPEHC
Standard Samples

Concentration of PE Ester (mole-%)		
Calculated	Found (HA-100)*	Found (A-60)*
0 †	3	4
2.1	5	6
4.9	6	11
10.0	12	16
24.9	28	26
50.0	53	52
75.0	75	78
90.0	90	91
95.0	93	95
98.0	99	98
100. ‡	-	100

*Standard deviation of the mean was $\pm 2\%$ or less.

†DPEHC reference sample.

‡PETC reference sample. PETC was used as a blank for the HA-100 analyses, hence its 100 Mc PE ester content is not listed.

Table 4
A-60 and HA-100 NMR Analyses of PETC-DPEHC-TMP
Standard Samples

Sample	Mole-% PE	Mole-% DPE	Mole-% TMP
1 Calculated:	33	33	33
Found (HA-100):	35	29	36
(A-60):	30	36	33
2 Calculated:	25	25	50
Found (HA-100):	27	24	49
(A-60):	29	24	47
3 Calculated:	45	45	10
Found (HA-100):	49	39	12
(A-60):	44	45	11

Because a TMP ester sample of known composition was not available, it was not possible to make as rigorous a test of the NMR method for determining TMP content. The molecular weight of NRL-T was determined by NMR (average acid chain length), and on this basis three samples containing varying proportions of PETC, DPEHC, and NRL-T were made. NMR analysis of the mixtures gave the results shown in Table 4. It appears that a ± 5 mole-% accuracy also holds for mixtures of all three components.

RESULTS

A group of lubricant formulations which were submitted for test under MIL-L-23699, as well as commercial ester stocks of NRL-S-300, NRL-S-304, NRL-S-302, and NRL-T were analyzed by the NMR method at both 100 Mc and 60 Mc in benzene solution. The quantitative results are listed in Table 5, with a reference to the figure showing the 100 Mc spectrum of each. Also given are the average acid chain lengths and degree of chain branching obtained by a method involving saponification of the esters followed by vapor-phase chromatography (VPC) analysis of the liberated acids (8).

Two of the oils contain TMP, one of them in significant quantity. The amount of TMP in the other is so small as to cause conjecture as to the reason for its presence; it may have been added for a small adjustment of viscosity.

CONCLUSIONS

The ease and accuracy (± 5 mole-% absolute) of the NMR method for quantitative assay of PE-DPE-TMP mixed esters indicate useful roles for it as (a) a means of monitoring base stocks, (b) a check on blend compositions, and (c) a means of determining the constancy of makeup of production batches of lubricant formulations which have qualified for military use.

The additional information from NMR concerning chain branching and average acid chain length can be used to detect moieties which may be undesirable.

Table 5
NMR Analyses of Commercial Ester and Lubricant Formulations

Sample	Fig.	Spectrometer	Concentration Mole-%			Av. Acid Chain Length		CH ₃ per Acid Frag.	
			PE*	DPE*	TMP*	NMR	VPC†	NMR	VPC†
NRL-S-300	8a	HA-100:	98	2	-	6.2	6.2	1.0	1.0
		A-60:	100	0	-	6.1		1.0	
NRL-S-304	7a	HA-100:	94	6	-	5.3	5.1	1.0	1.0
		A-60:	98	2	-	5.1		1.0	
NRL-S-302	7b	HA-100:	7	93	-	6.4	6.3	1.0	1.0
		A-60:	12	88	-	6.5		1.0	
NRL-T	4	HA-100:	-	-	100	8.8	-	1.0	-
		A-60:	-	-	100	8.9		1.0	
NRL-S-305	8b	HA-100:	79	21	-	6.4	6.1	1.0	1.0
		A-60:	85	15	-	6.1		1.0	
NRL-S-306	6a	HA-100:	4	24	73	7.7	7.5	1.0	1.0
		A-60:	3	22	75	7.8		1.0	
NRL-S-307	6b	HA-100:	83	8	10	6.9	6.6	1.1	1.2
		A-60:	84	8	8	6.9		1.1	
NRL-S-308	9a	HA-100:	74	26	-	5.8	5.5	1.0	1.0
		A-60:	71	29	-	5.6		1.0	
NRL-S-309	9b	HA-100:	89	11	-	6.7	6.4	1.2	1.2
		A-60:	85	15	-	6.5		1.2	

*Standard deviation of the mean was $\pm 2\%$ or less.

†Determined by saponification of the esters, followed by vapor-phase chromatography (VPC) of the liberated acids (8).

If higher absolute accuracy is desired, a calibration using mixtures of known composition can be made. It is estimated that an accuracy of ± 2 mole-% for each constituent would result.

The results obtained with an A-60 analytical NMR spectrometer and an HA-100 research NMR spectrometer are comparable in accuracy. Because the A-60 is by far the most common NMR spectrometer in use and its integrals are simple to process, it is felt to be the preferred instrument for routine quantitative determinations of PE-DPE-TMP mixed ester content.

ACKNOWLEDGMENTS

The authors are indebted to C.M. Murphy, P. Sniegowski, J.G. O'Rear, and H. Ravner of the Surface Chemistry Branch, Chemistry Division, NRL, for providing samples and for helpful discussions; and to E. Lustig of the Division of Food, Food and Drug Administration, for use of the A-60 spectrometer.

REFERENCES

1. "Lubricating Oil, Aircraft Turboprop and Turboshift Engines, Synthetic Base," Military Specification MIL-L-23699(Wep), June 6, 1963
2. Kraft, M.Ya., J. Chem. Ind. (Moscow) 8:507 (1931); Chem. Abs. 25:5114 (1931)
3. Wyler, J.A., Ind. Eng. Chem., Anal. Ed. 18:777 (1946)
4. Lew, B.W., Wolfrom, M.L., and Goepf, R.M., Jr., J. Am. Chem. Soc. 68:1449 (1946)
5. Jaffe, J.H., and Pinchas, S., Anal. Chem. 23:1164 (1951); Shay, J.F., Skilling, S., and Stafford, R.W., Anal. Chem. 26:652 (1954)
6. Carazzolo, G., Chim. e ind. (Milan) 42:858 (1960); Chem. Abs. 55:3009 (1961)
7. Wiersma, D.S., Hoyle, R.E., and Rempis, H., Anal. Chem. 34:1533 (1962)
8. O'Rear, J.G., and Sniegowski, P.J., "Analysis for Acyl Components of Neopentyl Polyol Ester Lubricants," NRL Report in preparation

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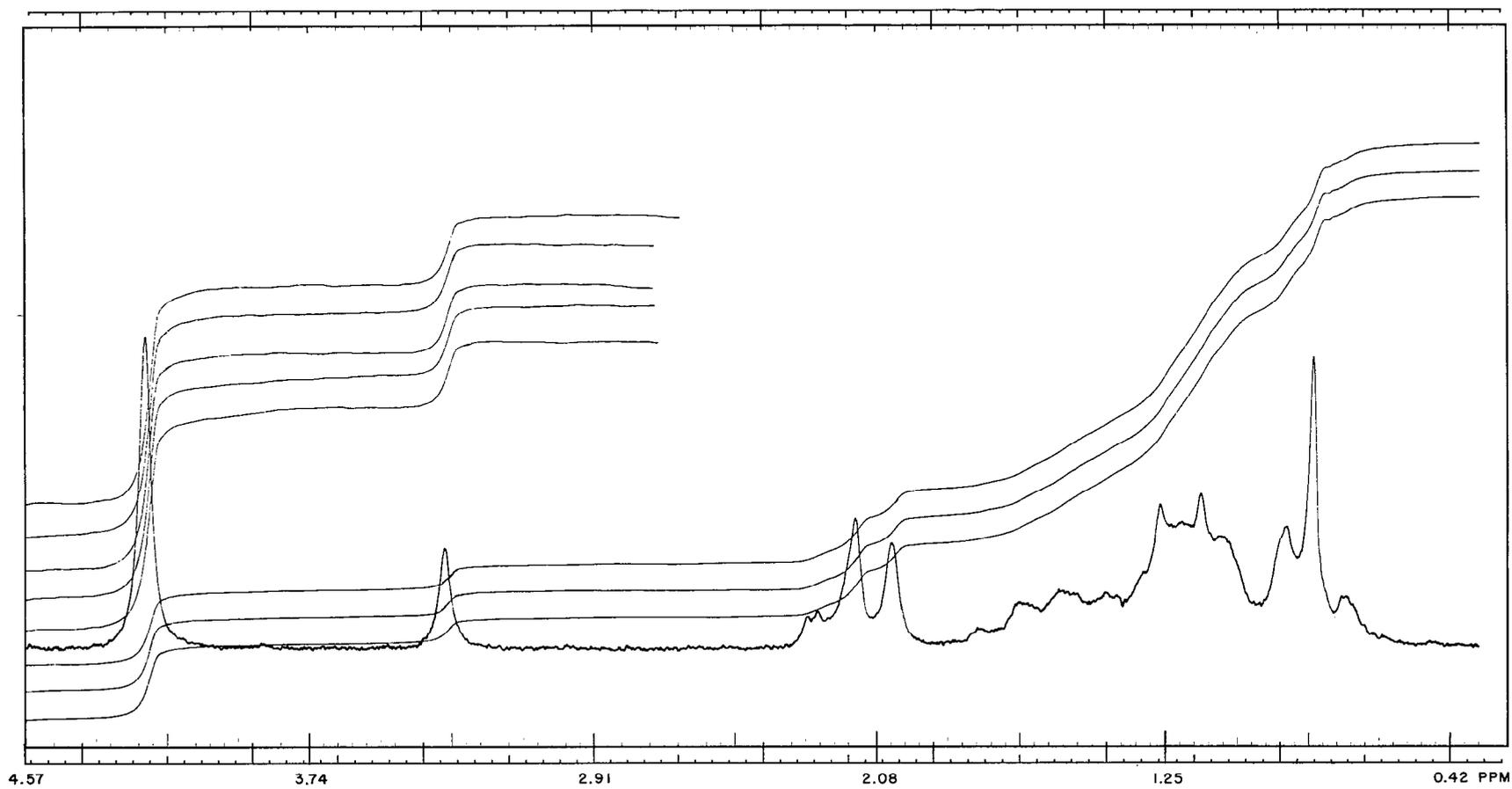


Fig. 1 - Typical A-60 spectrum and integrals (PETC/DPEHC Standard Sample No. 4)

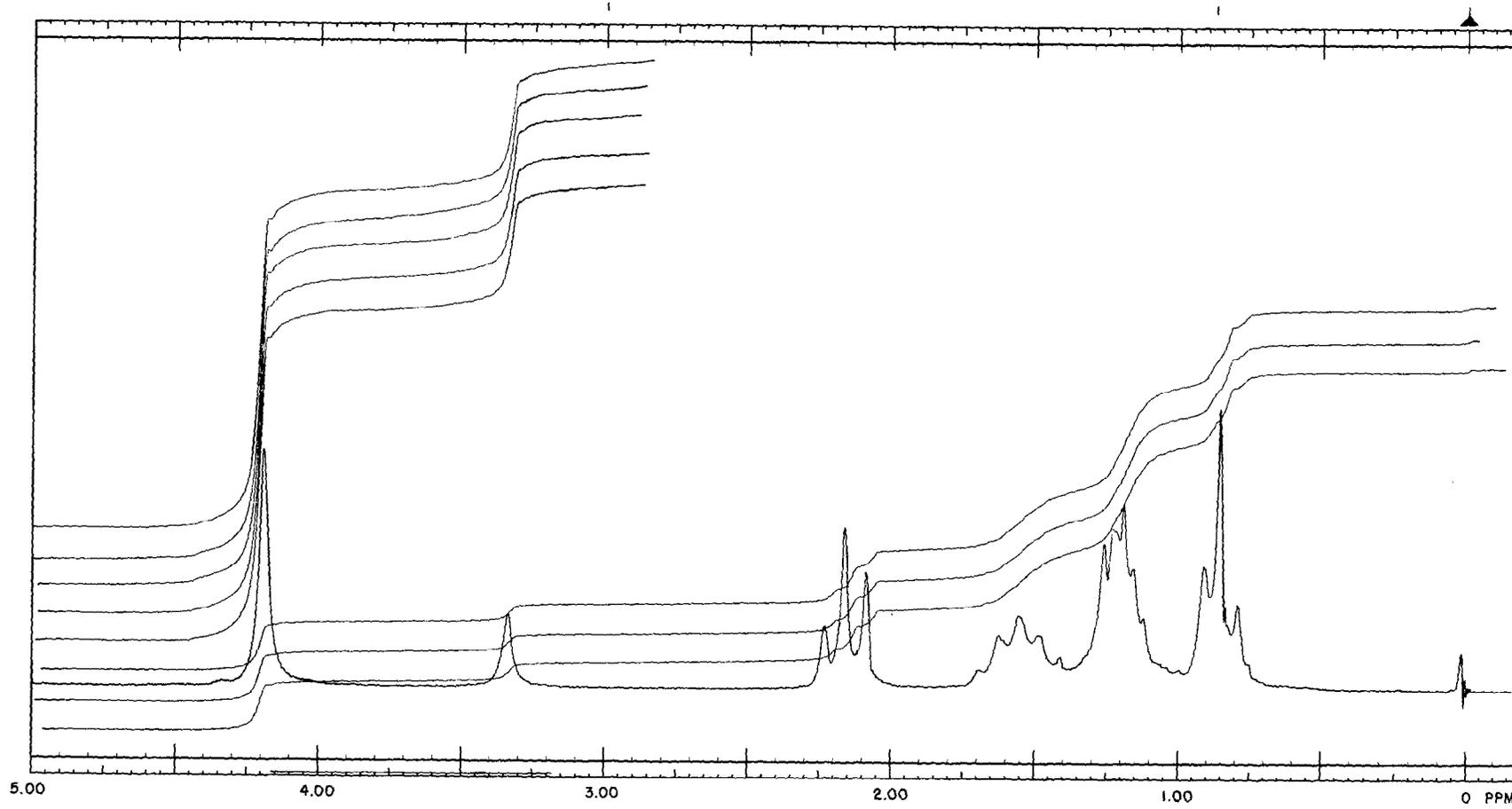


Fig. 2 - Typical HA-100 spectrum and integrals (PETC/DPEHC Standard Sample No. 4)

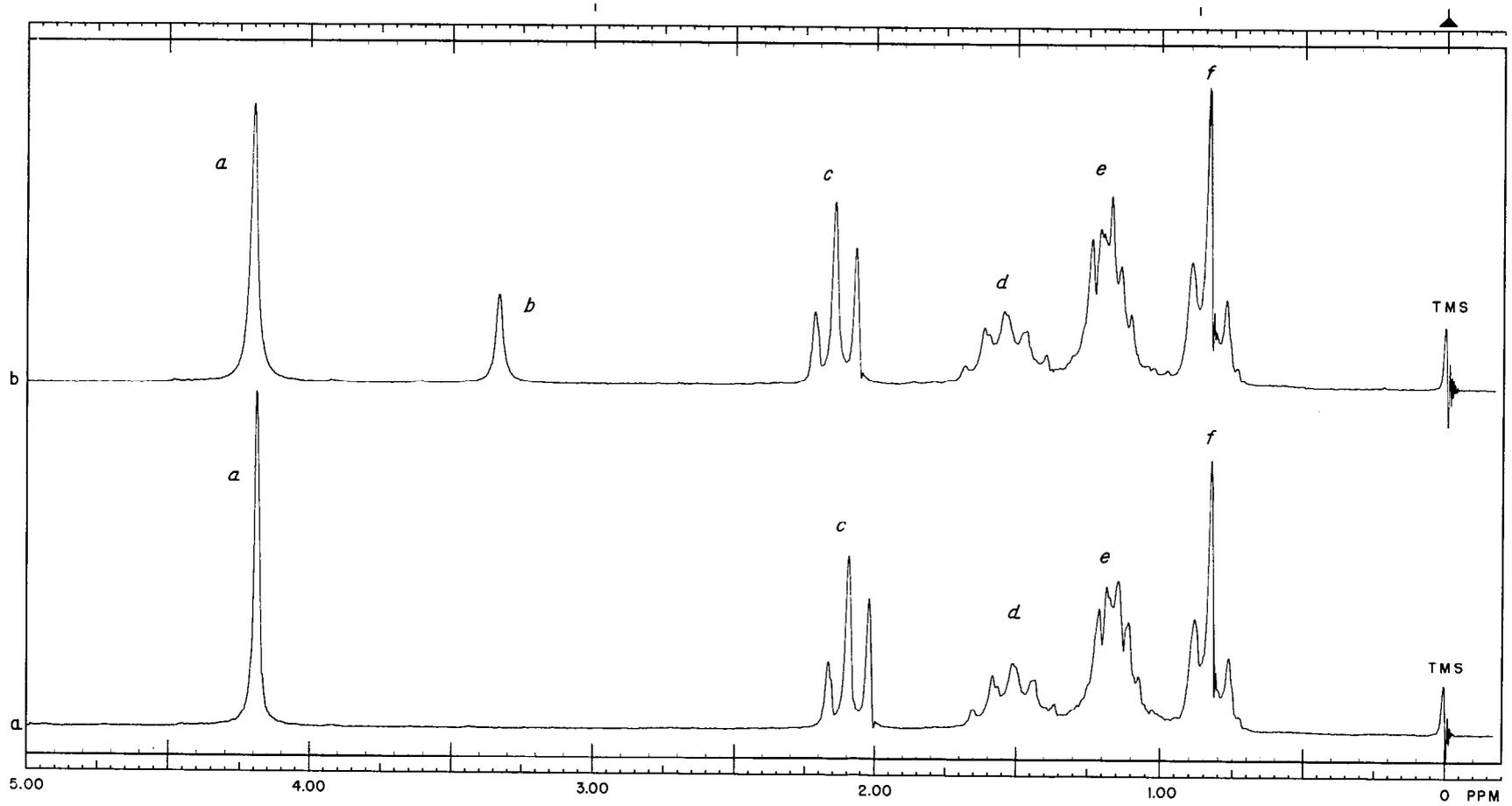


Fig. 3 - HA-100 spectra of (a) pentaerythritol tetracaproate (PETC) and (b) dipentaerythritol hexacaproate (DPEHC)

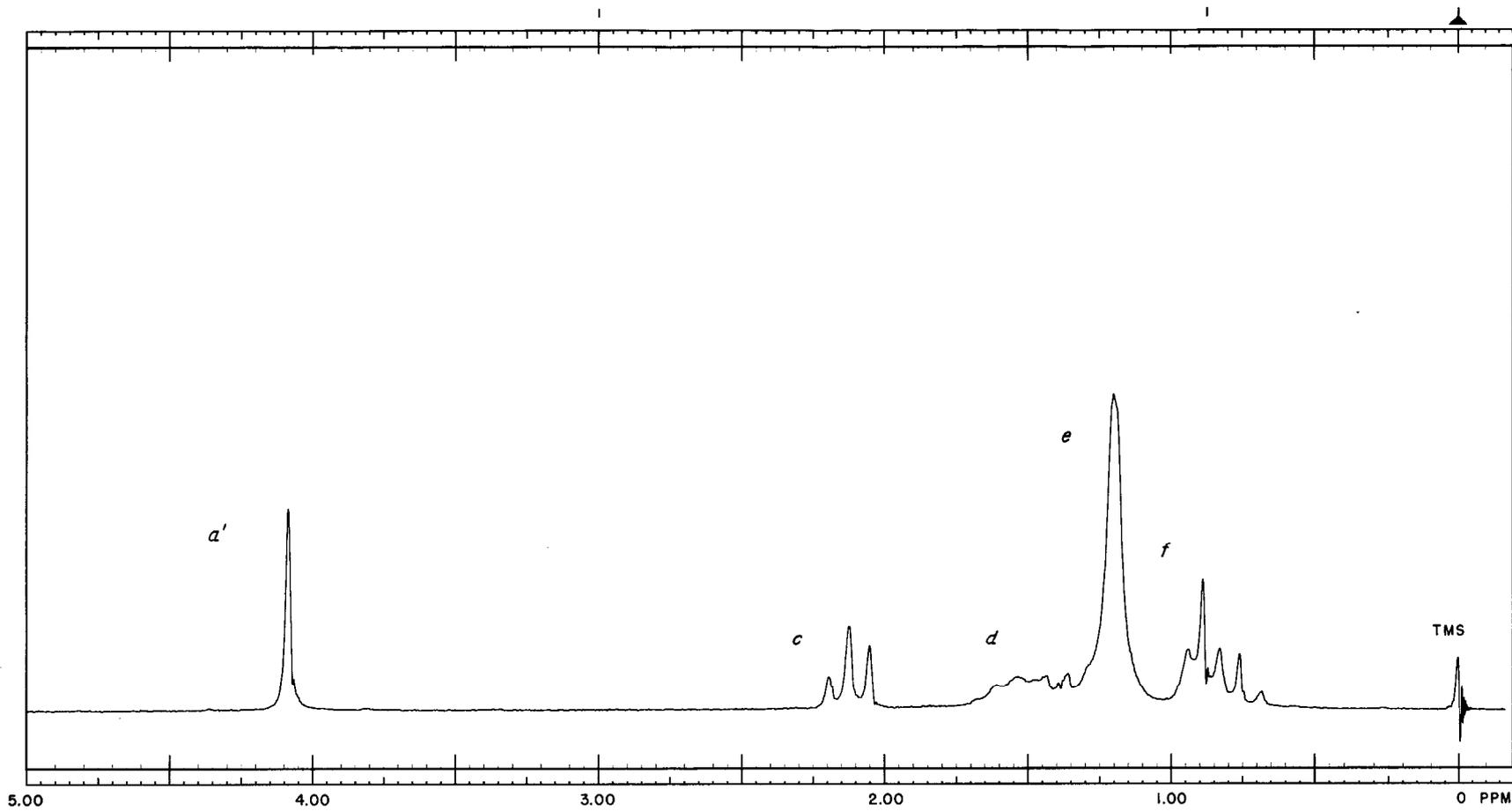
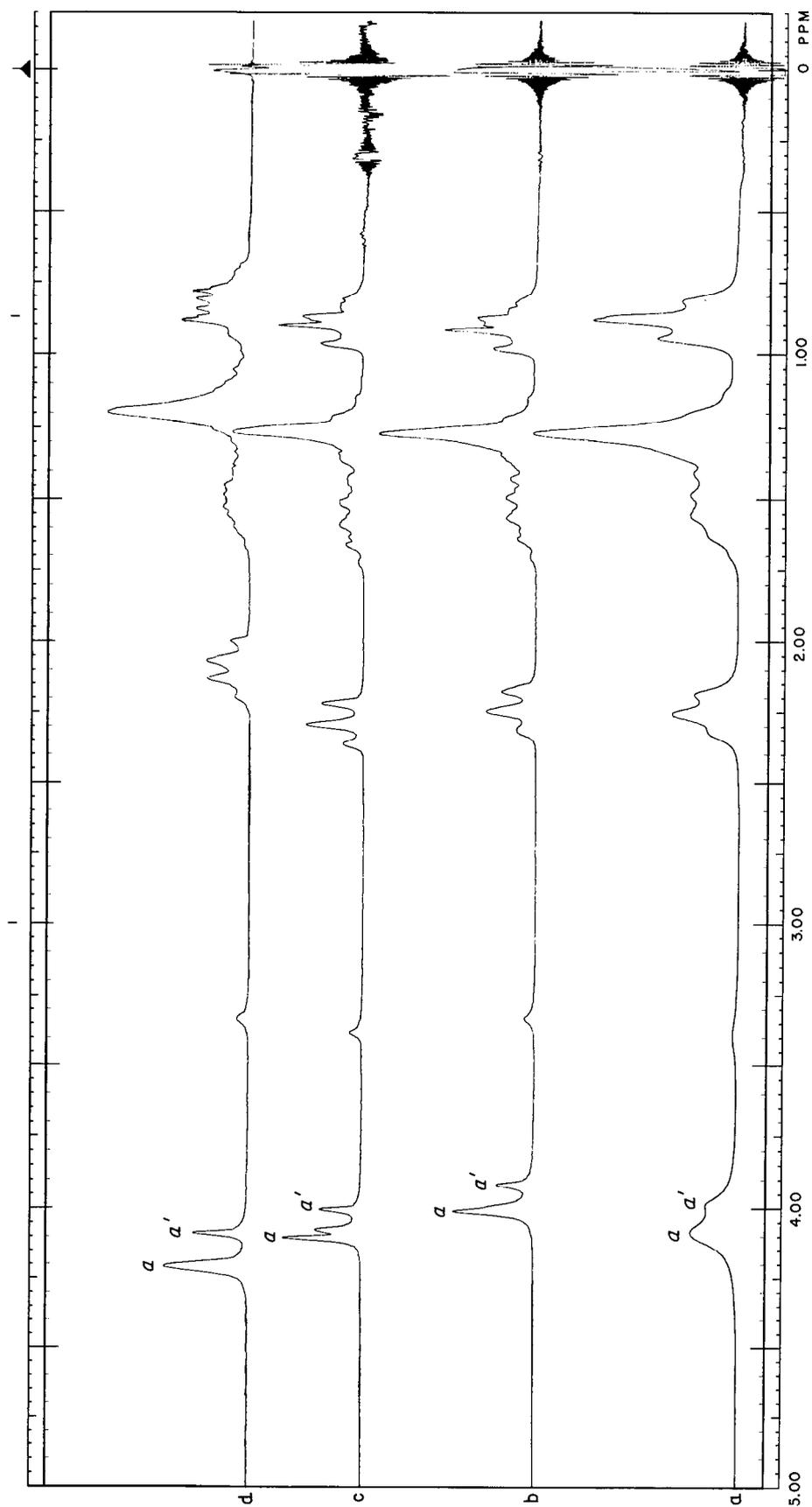


Fig. 4 - HA-100 spectrum of NRL-T



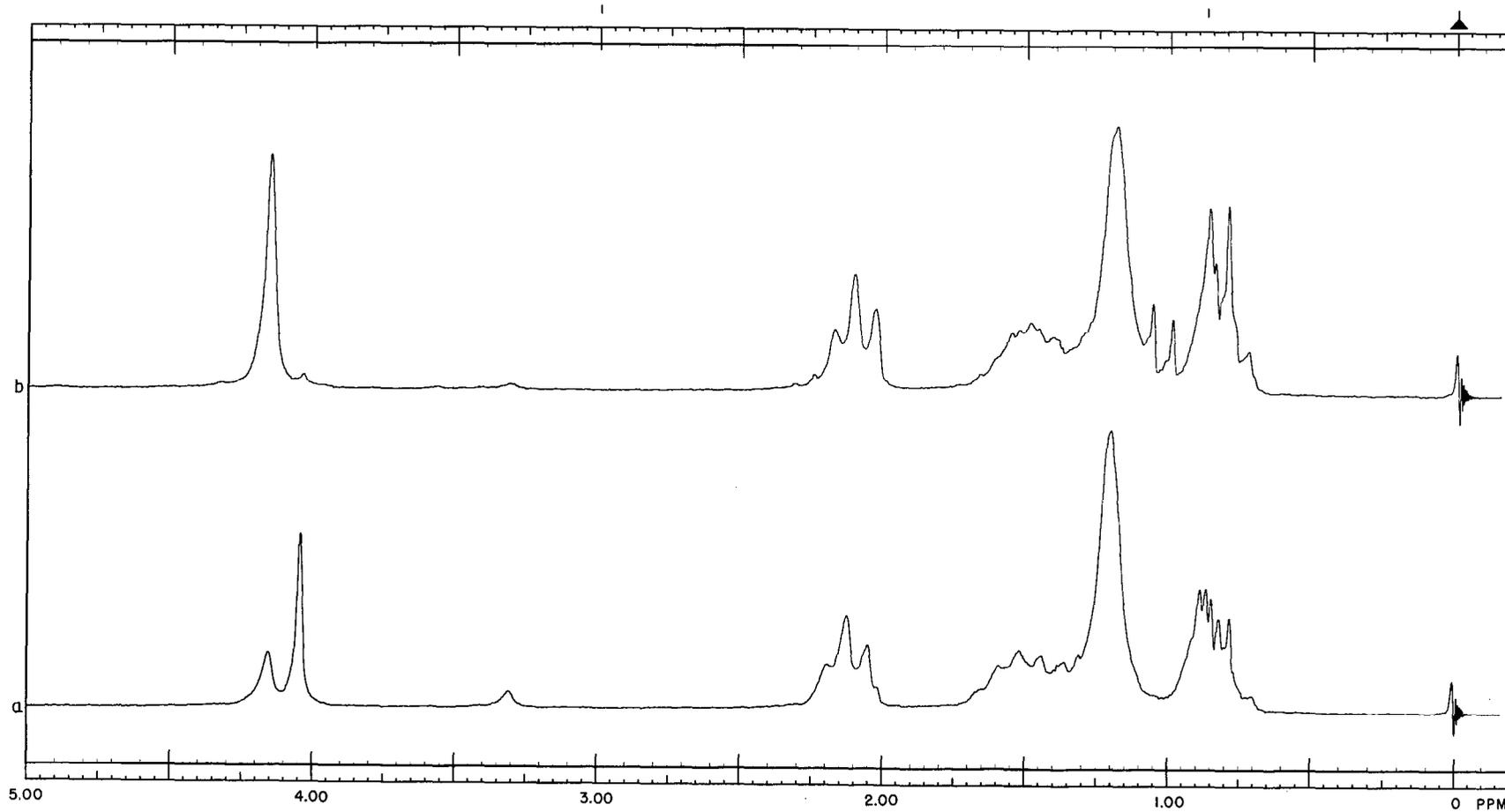


Fig. 6 - HA-100 spectrum of (a) NRL-S-306 and (b) NRL-S-307

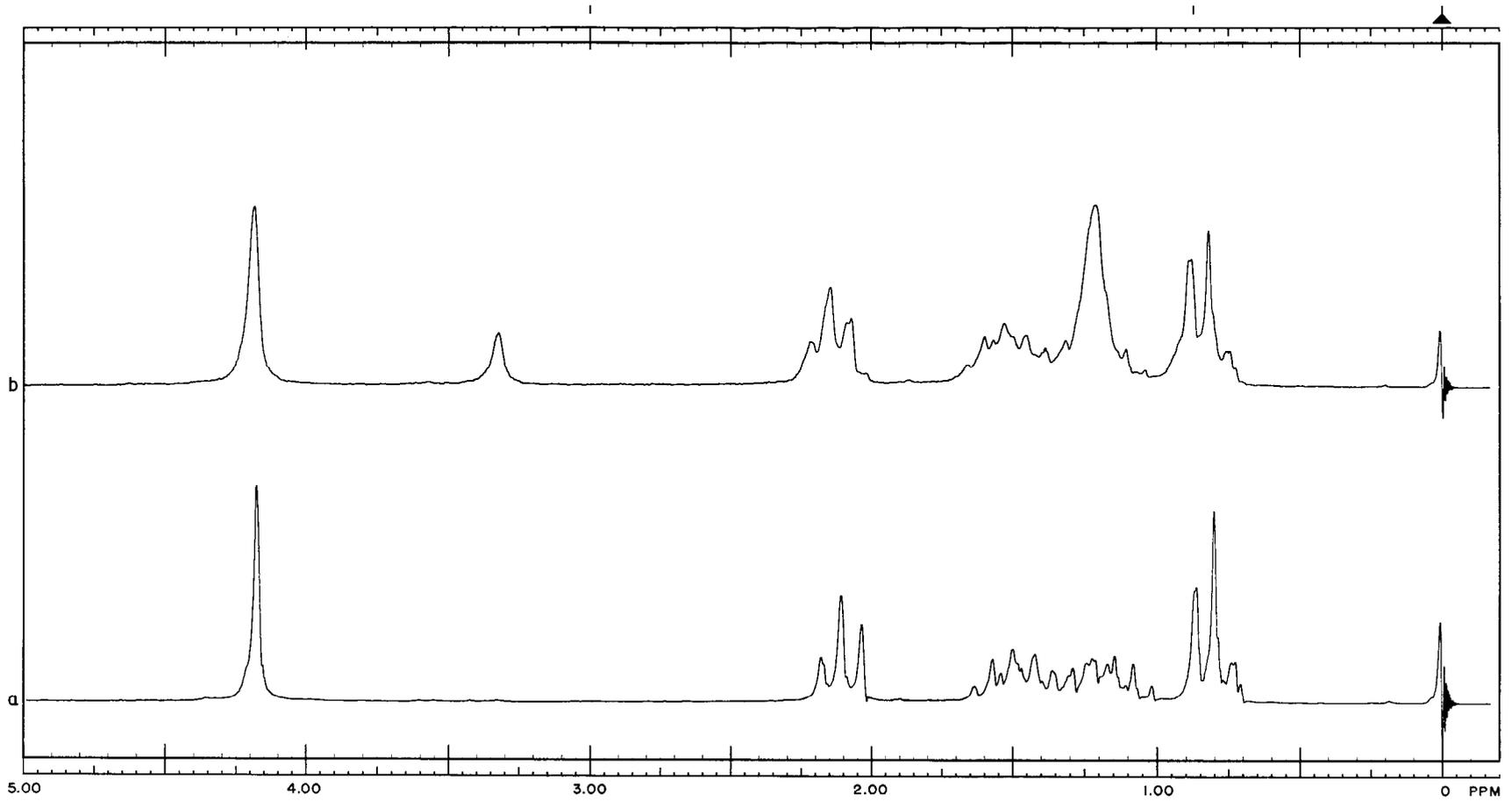


Fig. 7 - HA-100 spectrum of (a) NRL-S-304 and (b) NRL-S-302

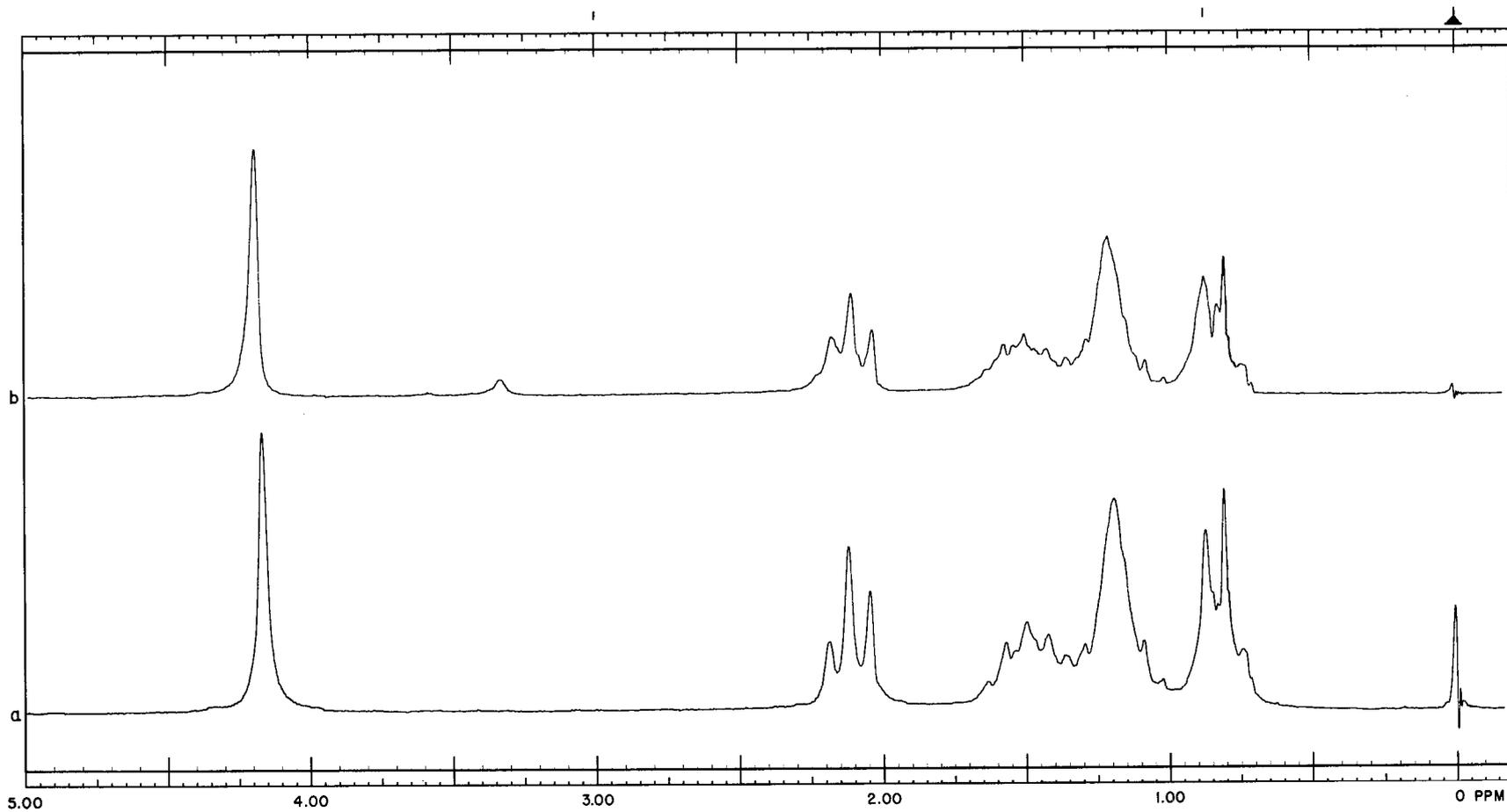


Fig. 8 - ¹H-NMR spectrum of (a) NRL-S-300 and (b) NRL-S-305

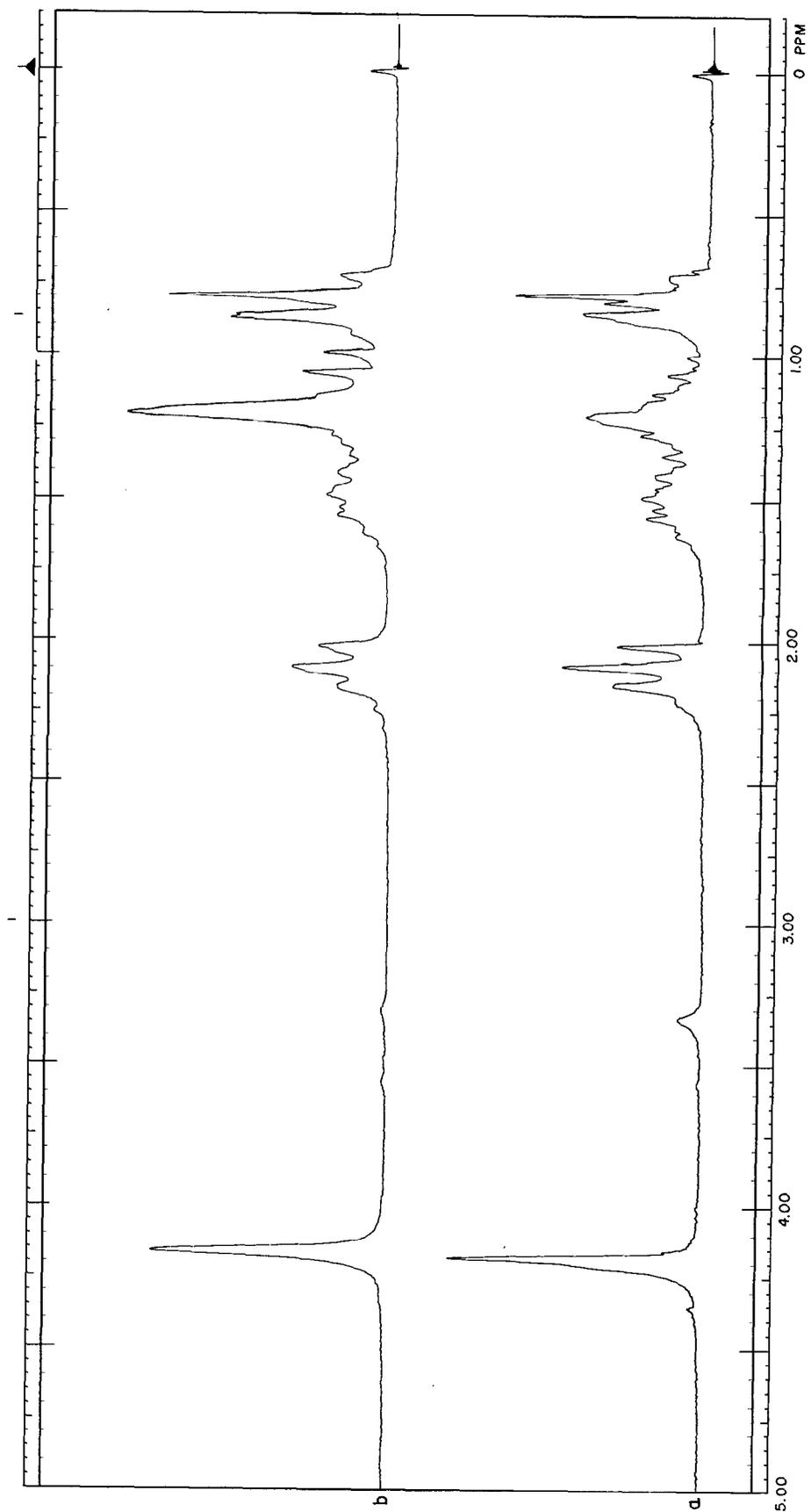


Fig. 9 - HA-100 spectrum of (a) NRL-S-308 and (b) NRL-S-309

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13. ABSTRACT <p>Benzene solutions of mixed pentaerythritol, dipentaerythritol, and 1,1,1-trimethylolpropane esters may be quantitatively assayed by proton NMR spectroscopy with an absolute accuracy of ± 5 mole-% for each of the ester types. Higher accuracies are possible if a calibration curve is used. - Average acid chain length and the approximate degree of chain branching are also obtained.</p> <p>The NMR method can be used for monitoring base stocks, checking blend compositions, and determining constancy of formulation of oils qualified under specification MIL-L-23699. NMR analyses of a group of commercial esters and of several aircraft engine lubricant formulations have been made. Results were obtained on both the Varian A-60 and HA-100 spectrometers, with comparable accuracy. The A-60 is felt to be the preferred instrument, however, because its integrals are simpler to process.</p>			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Nuclear magnetic resonance (NMR) Spectroscopy Nondestructive analysis Quantitative analysis Qualitative analysis Aircraft engine lubricants Military aircraft engine lubricants Pentaerythritol esters Dipentaerythritol esters 1,1,1-Trimethylolpropane esters						

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