

# NASA TECHNICAL MEMORANDUM

NASA TM X-62,411

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(NASA-TM-X-62411) . AMINO ACIDS IN A FISCHER  
TROPSCHE TYPE SYNTHESIS (NASA) : 10 -p HC \$3.25  
CSCL 06C

N75-21034

Unclas

G3/55 14684

## AMINO ACIDS IN A FISCHER TROPSCHE TYPE SYNTHESIS

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August 1974

1. Report No. NASA TM X-62,411	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle  AMINO ACIDS IN A FISCHER TROPSCH TYPE SYNTHESIS		5. Report Date	
		6. Performing Organization Code	
7. Author(s)  Donald L. Brown and James G. Lawless		8. Performing Organization Report No. A-5909	
		10. Work Unit No. 192-55-61-07	
9. Performing Organization Name and Address Department of Chemistry Santa Clara University and Moffett Field, Calif. Santa Clara, Calif. 95053 NASA, Ames Research Center 94035		11. Contract or Grant No.	
		13. Type of Report and Period Covered Technical Memorandum	
12. Sponsoring Agency Name and Address  National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code	
		15. Supplementary Notes	
16. Abstract  One postulation for the presence of organic compounds in meteorites is that they were formed during the condensation of the solar nebula. A viable laboratory simulation of these conditions can be modeled after the industrial Fischer Tropsch reaction, which is known to produce organic compounds called hydrocarbons. In this simulation, a mixture of carbon monoxide, hydrogen and ammonia is heated in the presence of iron meteorite. We examined the reaction products for amino acids, a class of organic compounds important to life. A large number of these compounds is found in meteorites and other chemical evolution experiments. Only small quantities of a few amino acids were found in the present simulation work. These results are at odds with the existing literature in which many amino acids were reported. Because of the relevance of this work, future laboratory simulations will be designed to maximize the yields of these compounds.			
17. Key Words (Suggested by Author(s))  Amino acids Chemical evolution Meteorites		18. Distribution Statement  Unclassified - Unlimited  STAR Category - 55	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 7	22. Price* \$3.25

## AMINO ACIDS IN A FISCHER TROPSCH TYPE SYNTHESIS

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The Oparin-Haldane (1,2) hypothesis of chemical evolution postulates that simple precursors formed complex organic molecules before life appeared on earth, and much experimental data has been obtained in the laboratory to support this hypothesis (3). This hypothesis could be further substantiated by a natural evidence for chemical evolution, and recently, a number of publications have appeared which indicate the indigenous nature of organic compounds in extraterrestrial samples, particularly meteorites (4-7). For the first time it appears possible to begin to define the organic compounds characteristic to an extraterrestrial abiotic synthesis. Because of the importance of amino acids to terrestrial life, much of the meteorite analyses has focused on these compounds (4,5,7). The apparent racemic nature of amino acids and the random distribution of structural isomers suggest that they are indigenous, and are not the result of contamination. These findings have induced others to look in more detail at the constituent amino acids produced by electric discharge through an atmosphere of  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_4\text{Cl}$  and  $\text{N}_2$ . (8,9) Many of the amino acids present in the meteorite were found in the electric discharge reaction, and it was suggested that the amino acids found in carbonaceous chondrites could have been produced on the meteorite parent body by a similar mechanism.

An alternative postulation is that these organic compounds were formed in the solar nebula during accretion (10). Anders and co-workers believed that a viable laboratory simulation of solar nebular conditions might be modeled after the industrial Fischer Tropsch reaction, which is known to produce hydrocarbons. They have therefore studied Fischer-Tropsch Type (FTT) reactions in which they heated a mixture of  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{NH}_3$  in the presence of iron meteorite. A number of amino acids have been identified as products of FTT reactions (11), however, in light of the more complex suites of amino acids found in meteorites and discharge experiments, we have examined several FTT reactions to determine if meteoritic amino acids could be accounted for by this process.

### Experimental

The FTT reactions were carried out in a quartz tube equipped with a 500 ml bulb, 4 ml vacuum stopcock, and a side tube for introducing catalyst and removing reaction products. During heating, the quartz tube was submerged to a depth of 9 cm in a tubular furnace while the remainder of the reaction flask was outside the furnace where reaction products could condense.

The catalysts, 300 mg of alumina and 200 mg of Canyon Diablo (CD) iron meteorite, were placed in the quartz tube and oxidized-reduced to remove organic contaminants. First oxygen gas at 1 atm was placed in the reaction flask and the catalysts were baked at  $700^\circ\text{C}$  for 7 hr. After reaction the oxygen was pumped off and hydrogen gas was introduced at 1 atm and the catalysts were reduced at  $400^\circ\text{C}$  for 4 hr. The Canyon Diablo meteorite was supplied by

Dr. R. Hayatsu, University of Chicago; the alumina was "Baker Analyzed" reagent grade chromatography support.

After oxidation-reduction of the catalysts, the reaction gases,  $\text{CO}:\text{H}_2:\text{NH}_3$ , were mixed in the reaction flask in a 1:1:1 molar ratio with a total pressure of 1 atm. For each FTT run, the tubular furnace was preheated to  $700^\circ\text{C}$  and the reaction flask was submerged in the furnace for 15 min. The flask was then quenched in air to about  $200^\circ\text{C}$  while at the same time the furnace was cooled to  $70^\circ\text{C}$ . Each flask was then reinserted into the furnace and allowed to bake at  $70^\circ\text{C}$  for 2-6 days. Table 1 lists the  $70^\circ\text{C}$  baking times for the seven FTT runs.

After heating, the reaction products were treated in three ways. The reaction flask was either extracted with water, extracted with acid, or extracted sequentially with both water and acid (see Table 1). In acid extraction, 50 ml of 6N HCl was refluxed in the reaction flask overnight under nitrogen atmosphere. Water extraction was carried out by introducing 50 ml of water into the flask and refluxing overnight. The supernatant was then separated from the solids and, in all but one run, the water extract was then hydrolyzed with acid. Hydrolysis of the water extract involved evaporating the water soluble fraction under reduced pressure and refluxing with 6N HCl overnight under nitrogen.

After acid extraction it was necessary to remove inorganic salts that formed from attack of the acid on the catalysts. Desalting was accomplished with cation exchange on Bio-Rad Dowex AG50W-X8, 50-100 mesh resin. The FTT samples were applied to a 65 ml column at a pH of 3.5; the column was washed with water until a test for chloride was negative, and then amino acids were eluted with 2N  $\text{NH}_4\text{OH}$ . Ammonia was removed by evaporating the sample under reduced pressure.

After removal of inorganic salts the amino acid samples were derivatized and analyzed by gas chromatography. Derivatization involved two steps (12). First the butyl ester was formed by reaction of the amino acids with anhydrous 6N HCl-n-butanol. The acid-butanol was refluxed with the amino acids for 1 hr. Excess acid-butanol was removed by evaporation under reduced pressure. In the second step the amino group was acylated using trifluoroacetic anhydride (TFAA) and  $\text{CH}_2\text{Cl}_2$  as solvent with a 10 min reflux.

In the derivatized form tentative identification of amino acids was made by gas chromatography (GC), on a 5% OV-17 glass packed column mounted in a Hewlett-Packard 5750 research chromatograph. Positive identification was obtained using a Perkin Elmer 990 gas chromatograph, equipped with a UCON 75H90000 capillary column, combined with a Dupont 21-491 mass spectrometer (GC-MS) by means of a membrane separator. A Decision, Inc., data system was used to acquire, store, and process the data.

Contamination was checked by simulating several FTT reactions without heat. This involved oxidation-reduction of the catalysts, introduction of the reaction gases as before, but without a heating mode, extraction of the reaction flask, and analysis of the extract for amino acids. A chromatogram of the water extract of a FTT blank run is shown in figure 1A.

The sensitivity of the analytical technique used in the FTT project was challenged by derivatizing 10 nanomoles of alanine, adjusting the total volume

of solvent ( $\text{CH}_2\text{Cl}_2$ ) to 50 microliters to yield an alanine concentration of 0.2 nanomoles/microliter, and injecting 1.0 microliter onto the gas chromatography column. One small peak was observed at the retention time corresponding to alanine.

## Results & Discussion

In run 1 the reaction flask was extracted with water only. It was assumed that the reaction products had condensed on the surface of the flask and catalyst, and that a simple water extract would remove them. The water extract was not hydrolyzed with acid. The extract was simply evaporated, derivatized, and analyzed by gas chromatography. No amino acids were observed.

In runs 2, 3, and 4 the reaction flasks were extracted with water. Each water extract was then hydrolyzed with acid to convert suspected precursors into corresponding amino acids and improve the yields of these compounds. Gas chromatograms showed small peaks, corresponding to amino acid retention values, but yields were so small that positive identification with mass spectrometry could not be made.

Run 5 was aborted due to contamination.

In run 6 the reaction flask was extracted sequentially with both water and acid. The water extract was then acid hydrolyzed, derivatized, and analyzed with gas chromatography. Figure 1B shows the chromatogram of the water soluble fraction of run 6. Amino acid peaks appear to be present but yields are too small for positive identification on mass spectrometry. The subsequent acid extraction of run 6 was performed in order to more thoroughly leach the reaction flask and catalyst (7).

In run 7 only an acid extraction was performed, which was then desalted, derivatized, and analyzed by gas chromatography. Yields were an order of magnitude greater so that positive identification using gas chromatography combined with mass spectrometry could be made. Figure 2 shows the total ion plot as a function of scan number for the acid extracts of runs 6 and 7. Positive identifications were made by matching mass spectra of unknowns and standards. Figure 3B shows the mass spectrum associated with scan number 285 of an unknown G.C. peak in run 7. This has been identified as N-trifluoroacetyl glycine-n-butyl ester by comparison with the mass spectrum of a known (figure 3A). In a similar manner several other peaks were identified. The total ion plots for the acid extracts of runs 6 and 7 are quite similar, however corresponding peaks don't occur at identical scan numbers because chromatographic conditions differed. In figure 2, peak 1 is trifluoroacetamide in both plots; peak 2 is alanine; peak 3 is leucine; and peak 4 is glycine in both plots. The large unidentified peak may be urea, but positive identification was not made using a standard. The presence of leucine, and none of the 4 or 5 carbon amino acids, suggests that run 7 might have some amino acid contamination.

A FTT reaction prepared by Hayatsu was also investigated by E. Peterson at the Chemical Evolution Branch, Ames Research Center. The deuterated reaction gases  $\text{CO}$ ,  $\text{D}_2$ , and  $\text{ND}_3$  were used to distinguish synthesized (deuterated) amino acids from contaminants. Only small amounts of deuterated alanine and glycine could be identified by GC-MS.

The presence of only small amounts of a few protein amino acids and no non-protein amino acids in our FTT experiments and Hayatsu's FTT reaction is

at odds with the literature (11). The reasons for this discrepancy are at present not understood, but because this type of experiment is important for our understanding of the nature of organic compounds present in meteorites, future laboratory simulations should be designed to maximize the yields of amino acids.

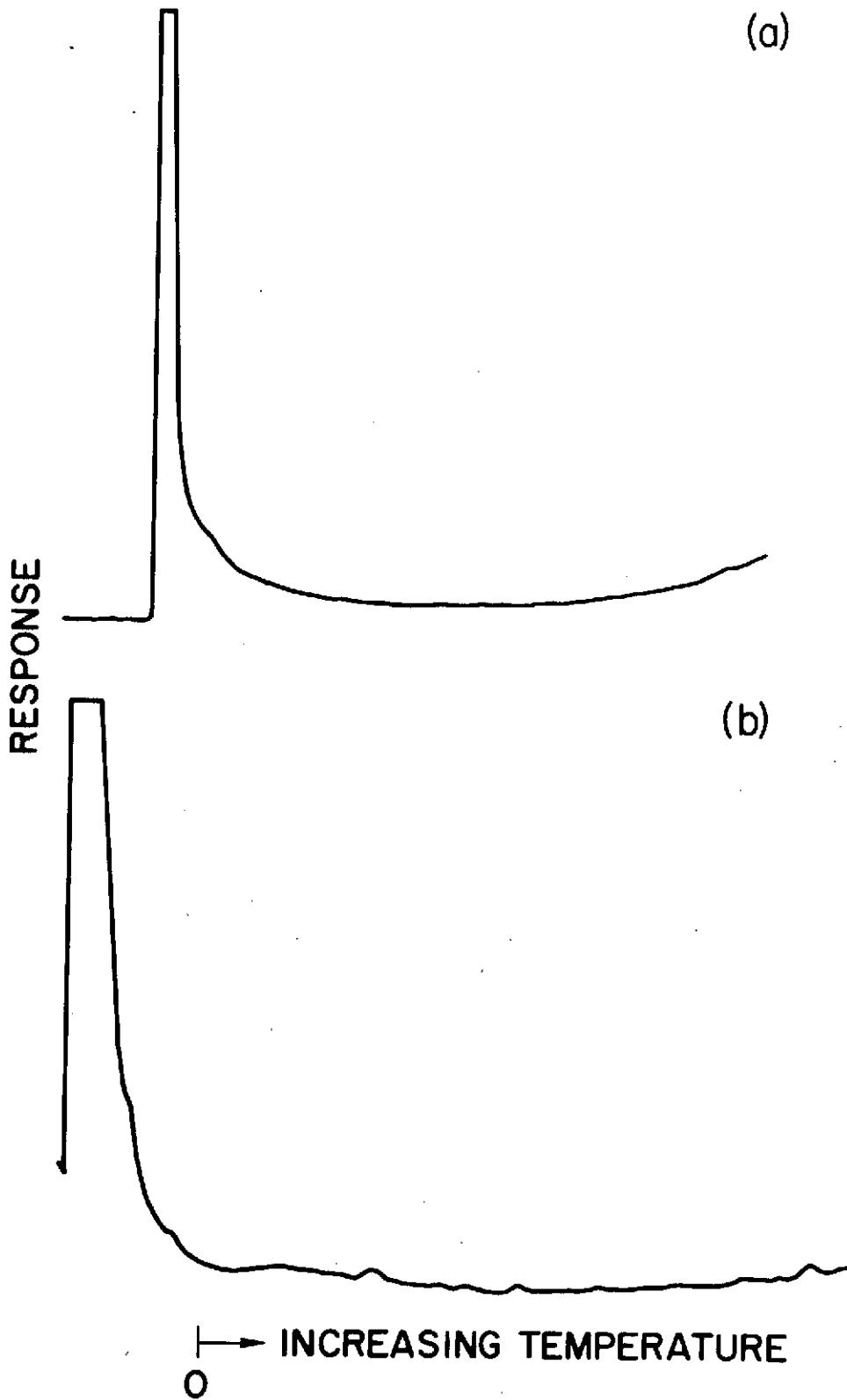
Acknowledgments. We thank Ms. J. Mazzurco and Mr. F. Church for their assistance.

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TABLE 1.- EXPERIMENTAL CONDITIONS.

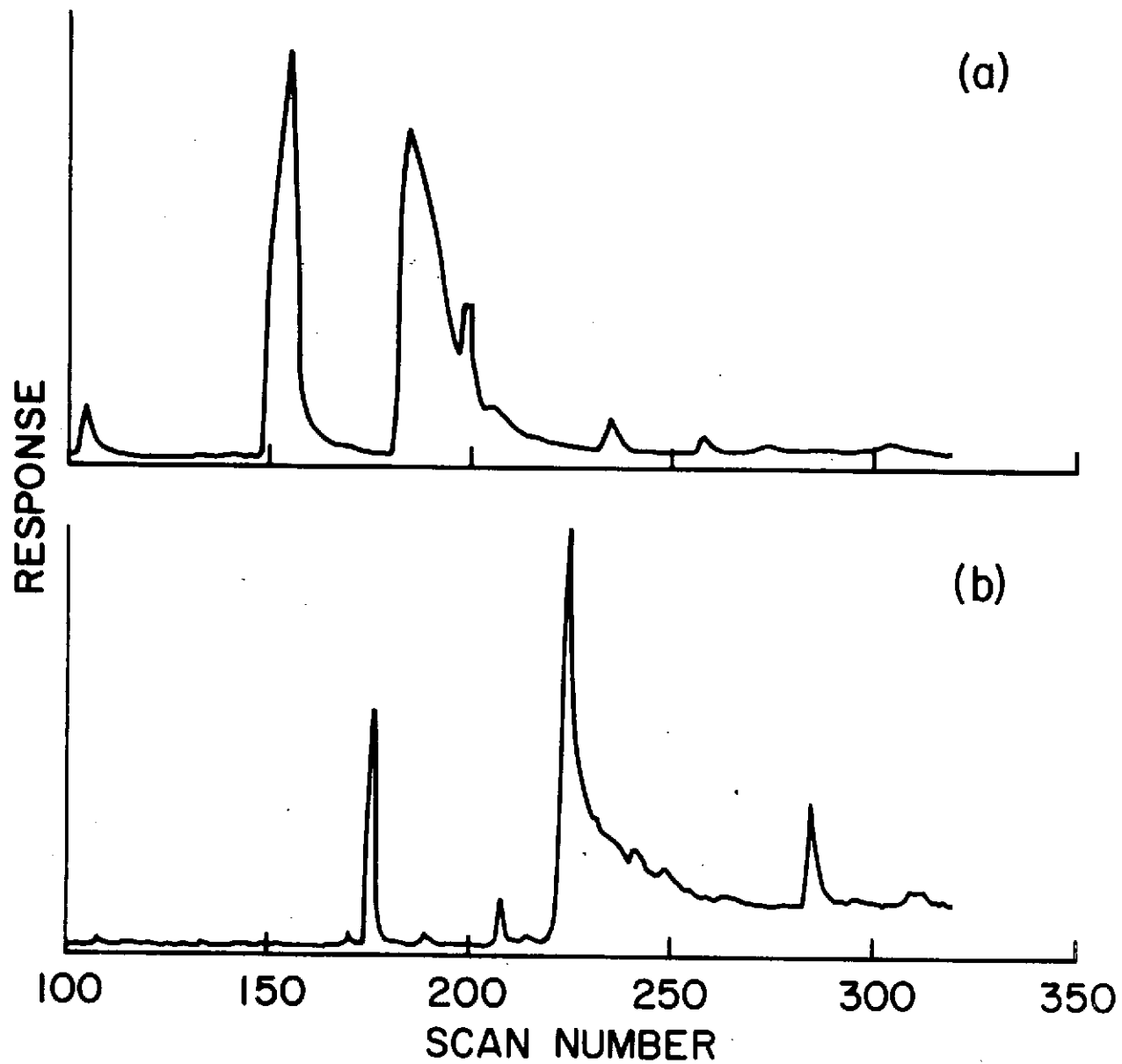
	Catalyst		Baking time (in hr.) at 70°C	Extraction Conditions		Water Extract Hydrolysis (6 N HCl) Conditions
	CD(mg)	Al(mg)		water t(hr)	6NHCl t(hr)	
R1	185.05	266.76	42	17	--	--
R2	225.53	315.18	117	27	--	16
R3	229.56	253.22	144	18	--	16
R4	201.53	340.46	65	16	--	16
R5	--	--	--	--	--	--
R6	200.85	305.26	64	48	16	264
R7	250.0	339.7	48	--	16	--



- (a) Derivatized water extract of the FTT blank run.
- (b) Derivatized water soluble fraction of FTT run 6.

Figure 1.- GC trace.

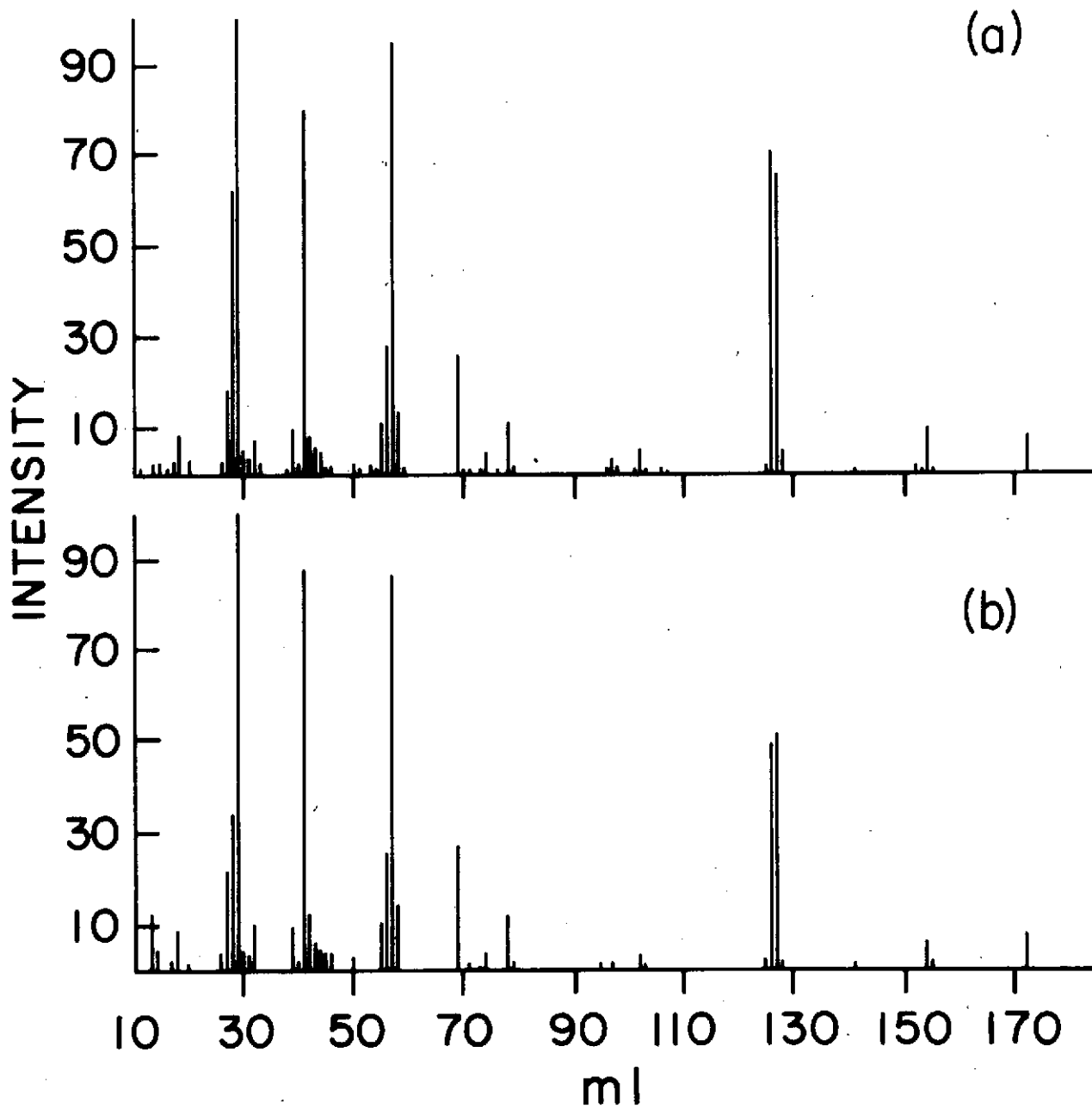




(a) Derivatized HCl extract of FFT run 6.

(b) Derivatized HCl extract of FFT run 7.

Figure 2.- Computer reconstructed total ion trace.



(a) Glycine standard as the n-butyl, N-trifluoro-acetyl derivative.

(b) Derivatized unknown from FTT run 7 (scan number 285).

Figure 3.- Mass spectrum.