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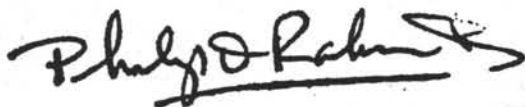
ORGANIC GEOCHEMISTRY ON THE JOIDES RESOLUTION—AN ASSAY

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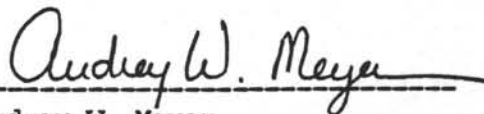
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PREFACE

"This will revolutionize geochemistry at sea," was the reaction of Dennis Graham, a chemistry technician with a long history in DSDP chemistry programs, after working--on the shakedown cruise, Leg 100 of the Ocean Drilling Program--in the Chemistry Laboratory of JOIDES Resolution. One of the main prerequisites for scientific advancement has always been the access to modern instrumentation, and the geochemical veteran cited above acknowledged the effort of ODP to provide a state-of-the-art laboratory for chemical work at the locus of interest: **the drill site**. Surpassing the main concern of shipboard organic geochemistry in previous phases of scientific ocean drilling, i.e. safety monitoring for hydrocarbons, geochemists onboard JOIDES Resolution are now able to analyze almost every property of sediments and rocks, ephemeral and resident, according to the modern analytical and data handling standards.

The following Technical Note is one of a series of three on geochemistry onboard JOIDES Resolution +). The demand for a concise description of tasks and supporting infrastructure for geochemical work onboard ship was the immediate reason for writing this series. Equally important was the desire to standardize methodology and to document geochemical work performed in the previous phases of scientific ocean drilling. They are intended to provide a guideline for shipboard geochemists, in order to facilitate their various duties.

The chemistry laboratory owes its tremendous potential to the advice and help of numerous individuals, who provided invaluable assistance in design and set-up. ODP acknowledges, in particular, the efforts of Drs. J.H. Brooks and M.C. Kennicutt II (Oceanography Department, Texas A&M University) in the planning stage; of Bradley Julson and Dennis Graham (ODP) for their activities toward setting up the laboratory in its present great shape; of Drs. Keith Kvenvolden (U.S.G.S., Menlo Park), Jorge Gieskes (Scripps Institution of Oceanography), Kay Emeis (ODP), Mr. Thomas McDonald (Oceanography Dept., TAMU), and Ms. Gail Peretsman (ODP), who were responsible for setting up the methods and procedures for the chemistry laboratories and writing these reports; and of Ms. Katie Sigler, Ms. Gail Peretsman, Ms. Tamara Frank, Mr. Matt Mefferd, Mr. Larry Bernstein, and Mr. Bradley Julson, for their roles in the maintenance and operation of the chemistry equipment at sea. Without the efforts of all of the above persons, the chemistry at sea program would not have reached its present highly successful state.

- +) Gieskes, J.M., and Peretsman, G., 1986. Water Chemistry Procedures aboard JOIDES Resolution. ODP Technical Note #5.
Kvenvolden, K.A., and McDonald, T.J., 1986. Organic Geochemistry on the JOIDES Resolution -- An Assay. ODP Technical Note #6.
Emeis, K.-C., and Kvenvolden, K.A., 1986. Shipboard Organic Geochemistry on JOIDES Resolution. ODP Technical Note #7.



Philip D. Rabinowitz, Director
May 1986

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I. INTRODUCTION

The chemical laboratory aboard the JOIDES Resolution is a modern, state-of-the-art facility providing an impressive capability for both organic and inorganic geochemical analyses. At the request of the Ocean Drilling Program (ODP), we have attempted to evaluate the organic geochemical aspects of this laboratory in order to provide some recommendations and suggestions for the future. As a start, we reviewed the report of Gieskes and Peretsman (1986) which considered the inorganic geochemistry capabilities on this ship. This report dealt with the procedures used on Leg 102 in the measurement of routine parameters for determining pore water chemistry. We realized that our report could not follow the same format because, at present, there is no established, shipboard protocol for routine organic geochemical measurements. Only the determination of hydrocarbon gas compositions is required by ODP when gassy cores are recovered, and these measurements are not done routinely except as needed for safety considerations. Thus, our report will discuss possible routine, organic geochemical measurements which should be made as part of the shipboard chemical program and will recommend equipment necessary to make the measurements. We will discuss the instrumentation presently available for the recommended routine program, and will consider additional instrumentation needed for that program. Our recommendations will be tempered by the fact that bench space in the laboratory is at a premium. The laboratory is already crowded, and there is little room for expansion. There is not sufficient laboratory space to lay out data, and space within the hoods is very precious. Scientists participating on future legs may have difficulties finding room in the chemical laboratory for any specialized, large items they may need to bring on board.

Besides considering a routine organic geochemical program, we will also describe briefly all of the instruments currently available for organic geochemistry in ODP. Because we have had an opportunity on Leg 104 to utilize these instruments and the supporting computerized data analysis systems, we will comment on some of the procedures that worked well for us. We will also point out some of the problems that we experienced. We do not claim that our procedures are optimum, but at a minimum, they should provide a starting point for future participating scientists, who no doubt will have newer and better ideas of how things should be done.

As a part of the program for Leg 103, potential organic geochemical contaminants on the ship were collected and analyzed (Dunham, in press); we have expanded this collection, and we present the results of our analyses as part of this report (Appendix A). Each potential contaminant has a distinctive gas chromatographic pattern, and these patterns should be useful in distinguishing shipboard-related petroleum substances from natural, petroleum-related materials which may be encountered during core recovery.

During the 47 days of Leg 104 we had the chance to become very familiar with much of the chemical laboratory of the JOIDES Resolution. It was a great pleasure to work with the new instrumentation and data support systems. Throughout our efforts we had the dedicated interest of the ODP Chemists, Gail

Peretsman and Katie Sigler, who contributed significantly to making this report possible. We thank ODP for the opportunity to participate on Leg 104.

II. SUMMARY OF LAB STATUS

The chemical laboratory aboard the JOIDES Resolution is well equipped to carry out basic studies in organic geochemistry, but additional instrumentation will be needed to implement an efficient, routine monitoring program. Such a program is recommended and described. It involves (1) regular sampling at approximately 30 m intervals and (2) analyses of the collected samples for hydrocarbon gases and organic carbon. The results of this program will yield valuable information for both science and safety.

Modern instrumentation for organic geochemistry in the laboratory includes two gas chromatographs, an elemental analyzer, a specialized pyrolysis system, and a carbonate carbon apparatus. The gas chromatographs interface with a laboratory automation system. Software used in conjunction with this system provides capabilities of integrating and plotting chromatographic data. To the instrumentation now available, we have recommended the addition of a small gas chromatograph specifically for the rapid measurement of methane and ethane. A total carbon apparatus is also needed for the accurate and precise determination of organic carbon.

We identified potential organic geochemical contaminants and provide a catalogue of gas chromatographic "fingerprints" (Appendix A). These chromatographic patterns should be useful in safety monitoring and in giving geochemists a means of detecting contaminated samples.

This chemical laboratory has tremendous potential. The results to be expected in the coming years will undoubtedly advance the field of organic geochemistry and add to our knowledge of the organic geochemical processes taking place in oceanic sediments. The only constraints on this advancement will be those imposed by operations at sea.

III. ROUTINE MONITORING FOR ORGANIC GEOCHEMISTRY

At present there is no clearly defined, routine program of organic geochemistry in ODP. This situation contrasts with that of the ODP inorganic geochemistry program which has its roots extending as far back as DSDP Leg 35 (Gieskes and Lawrence, 1976). In the inorganic program the following parameters are measured routinely in pore waters squeezed from sediment samples: alkalinity, salinity, pH, cations of calcium, magnesium, and potassium and anions of sulfate and chloride. These parameters are generally ephemeral, and must be determined immediately on shipboard or else the information will be forever lost. The wisdom of collecting these data has been verified by the increased knowledge that has been gained concerning the chemical processes

taking place in oceanic sediments (e.g., Gieskes, 1981).

Organic geochemists have been remiss in not insisting that important organic geochemical measurements be routinely made as part of DSDP and now ODP. Routine sampling for organic geochemistry (30-cm long whole-round core sample every 30 m of recovered core) is already a part of ODP, but routine, chemical measurements are not. The problem is that there is no consensus as to what should be measured and how it should be done. To attempt to move forward toward a routine shipboard organic geochemical program, we will propose the measurement of two parameters, one ephemeral and one not. We believe that low-molecular-weight hydrocarbons from methane to at least the pentanes are significant constituents of oceanic sediments; they are for the most part ephemeral. These compounds, especially methane, are also important from the point of view of safety. The second parameter that should be measured is organic carbon. Organic carbon is not an ephemeral property of sediments, but knowledge of its concentrations is very useful in interpretation of paleoenvironments and is also considered in evaluations concerning safety.

A. LOW-MOLECULAR-WEIGHT HYDROCARBONS

Low-molecular-weight hydrocarbons, hereafter referred to as hydrocarbon gases, are ubiquitous in oceanic sediments (Claypool and Kvenvolden, 1983). Considerable scientific knowledge already exists regarding the molecular and isotopic compositions of these gases, and much of this information has resulted from DSDP sampling. At present ODP requires that gas compositions be monitored only when gassy cores are recovered. This procedure is essential for safety considerations, but does not provide a complete picture of the distribution and origin of light hydrocarbons in sediments. We believe that hydrocarbon gases should be measured routinely in ODP sediment cores, and that sampling should begin in the first core of every hole and continue at a minimum in every third core to total depth. This sampling scheme would provide at least 3 data points every 100 m which should yield enough information to establish trends in compositional changes with depth.

G.E. Claypool, Chairman of the JOIDES Pollution Prevention and Safety Panel, has also recommended that ODP evaluate and upgrade the shipboard hydrocarbon monitoring procedures. In his letter addressed to L.E. Garrison, dated February 22, 1984, Claypool writes "In the past, there has not been a standard set of procedures for routine hydrocarbon monitoring. . . I believe that a technique for the rapid analysis of C₁ - C₅ hydrocarbons in sediments should be developed for systematic use in the new drilling program". Although Claypool's concern is mainly safety, a well-designed, routine procedure can serve science as well.

Assuming that we have adequately established the need in ODP for a routine monitoring scheme for hydrocarbon gases, we now address the issue of a procedure. No one is sure of the best way to do this analysis. The hydrocarbon gases are very volatile, and, without a pressure core barrel, it is impossible to determine their in situ concentrations. What is now measured upon core recovery is the residual gas much of which is dissolved in the pore

fluids or adsorbed to sediment particles. But even this residual gas is important geochemically and is useful in safety evaluations.

There are at least two possible procedures for use in monitoring hydrocarbon gases. One is a headspace analysis and the other involves hydrogen stripping. There are precedents for both methods. As early as DSDP Leg 18, McIver (1973) used a headspace method for the analysis in his shorebased laboratory of samples collected at sea. More recently the method was used on the Glomar Challenger on Leg 76 (Kvenvolden and Barnard, 1983) and Leg 84 (Kvenvolden and McDonald, 1985), and on ODP Leg 104. The hydrogen stripping method was used on samples collected on Leg 71 (Schaefer et al., 1983) and Leg 75 (Schaefer and Leythaeuser, 1984). The method was used on shipboard on Leg 79 (Shipboard Scientific Party, 1984) and in a shorebased laboratory on samples collected on Leg 79 (Schaefer et al., 1984). We discuss the methodology, advantages, and disadvantages of both methods below.

1. Headspace Analysis

The procedure for headspace analysis is very simple and involves taking a 5-cm long whole-round section of core (about 160 cc) and extruding the sediment into a 1 pint can previously prepared with septa. To the can is added helium-purged water, and a 100 cc headspace is established. The can is sealed, and the headspace purged with helium. Gases are extracted into the headspace by shaking the can for 10 min on a mechanical, high-speed shaker. A portion of the headspace gas is analyzed by gas chromatography. For a routine shipboard program, the helium purge of water and headspace might be eliminated thus simplifying the method even more. If the purge is eliminated, then blanks (using a can of water with a 100 cc headspace) should be run each day that samples are being analyzed, and the results subtracted from the results obtained on samples. The ambient background in the blanks should be low, and only important when concentrations of gases in the samples are correspondingly low. When gassy cores are sampled, the blanks should not be a problem.

Comparisons of results from headspace analysis of sediments with the results from direct analysis of gas in gas pockets of cores show some important similarities as well as differences. Although the concentrations of gases in a gas pocket exceed the concentrations of gases recovered by headspace analysis of a sediment sample taken near the gas pocket, the ratios of gases in the two mixtures are similar. For example, at Site 533 the ratios of methane/ethane from headspace analysis of sediments and from gas pockets show similar trends (Shipboard Scientific Party, 1983; Fig. 1). The absolute ratios are slightly and consistently lower in the headspace results. This example illustrates that trends in ratios of gases obtained by headspace analysis can be as useful as trends measured from gases in gas pockets. Because headspace analysis depends only on having a sediment sample and not on the presence of gas pockets in the core, the method can be used throughout an entire sediment core.

The main advantage of this method is its simplicity. The disadvantages are large sample size (160 cc of core) and the fact that all of the gases are not recovered for analysis. Gases partition between the headspace and the water-

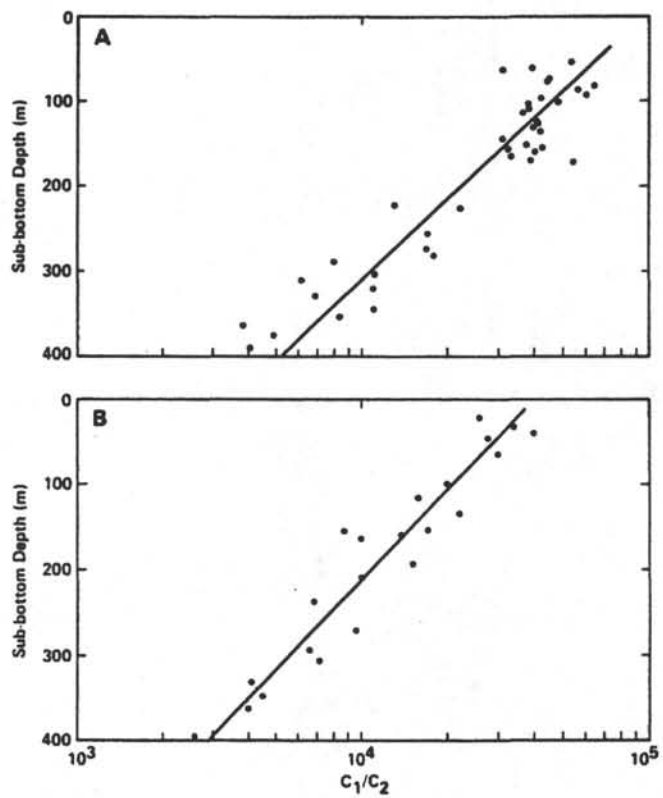


Figure 1. Methane/ethane (C_1/C_2) ratios at DSDP Site 533:
 A. Ratios obtained from analyses of gases in gas pockets.
 B. Ratios obtained by headspace analyses.
 From: Shipboard Scientific Party, 1983, p. 61.

sediment mixture, and partition coefficients for the gases are not well established and vary with different sediment types. Nevertheless, the results obtained by this method provide information that is directly comparable with data from the direct analysis of gases in gas pockets.

2. Hydrogen Stripping

This procedure has been applied successfully in the recognition of source rocks and assessment of petroleum generation potential. The method (Schaefer et al., 1978) is a single step procedure carried out in a gas flow system (Fig. 2). A small amount of freshly crushed sediment sample (about 1 to 10 g) is placed in the flow system of a capillary gas chromatograph with hydrogen carrier gas serving as the stripping gas. The sediment is heated simultaneously to 110° C for 5 min in a hydrogen flow of 5 ml/min. Prior to chromatography, the contents of the flowing hydrogen are filtered to remove water. The claim is made that the yields obtained represent nearly the absolute quantities of light hydrocarbons present, both dissolved in the pore water and adsorbed on mineral surfaces (Schaefer et al., 1984).

Claypool in his letter to Garrison (cited earlier) wrote that the hydrogen stripping technique has "provided the most meaningful set of light hydrocarbon analyses ever obtained in the Deep Sea Drilling Project". He recommended that the method be adapted for routine shipboard monitoring of hydrocarbon gases.

In theory this method looks very promising. Its advantages include very small sample size (1 to 10 g), simplicity, and quantitative removal of gas. The disadvantages include the use of hydrogen, a hazardous material especially on a ship, for stripping, and the fact that methane (C₁), a most important gas, is not measured. The method is useful for ethane through about nonane (C₂ - C₉).

3. Suggestions for Routine Analyses

Neither the headspace nor hydrogen stripping procedure is an ideal method for routine shipboard work. Perhaps with modifications one or the other of these methods could be improved for shipboard use. The following recommendations are made as a point of departure:

(1) The headspace method should be used immediately by ODP for routine monitoring of hydrocarbon gases. The only additional equipment needed is a paint-can shaker in an enclosed container to reduce noise. Samples (5-cm long whole-round cores) should be taken at least every third core starting with the first core (avoiding the core from which the 30-cm long organic geochemical sample is routinely taken. This sampling will reduce the amount of sample taken from any given core. To simplify things, the samples can be processed without helium purging, and 1-pint paint cans (some are already on the ship) can be used. A methane blank of about 3 ppm can be expected, however, if helium purges are not used. This number is the ambient methane concentration we measured in the laboratory air.

A septum can be attached to the can prior to sampling by punching a hole in the can near the top and gluing the septum in place with silicone cement. This process should be done at least two days before sampling, and the cans

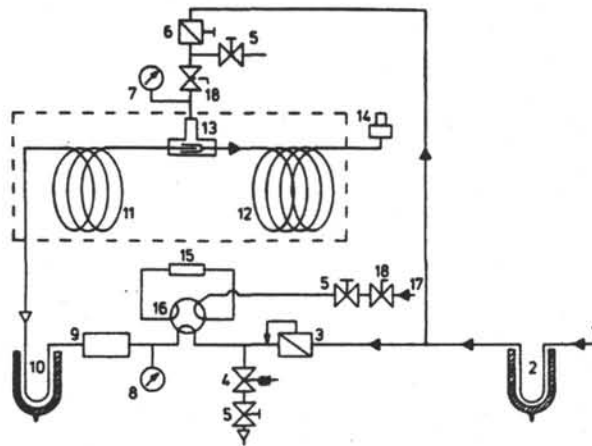


Figure 2. Modified capillary gas chromatographic system for light hydrocarbon analysis of sediment samples by hydrogen stripping (Schaefer, Weiner, and Leythaeuser, 1978).

should be left open until the cement is dry and all vapors have escaped. A blank sample should be run each day of sampling utilizing the same water that is put in the cans with the samples. After an analysis is made the can should be opened, and its contents placed in a plastic bottle for curatorial purposes. Later the water can be removed by filtration. Storage in the cans is not recommended because the cans will eventually rust, and the gas mixture inside will likely be modified especially by microbial processes. This procedure of sample storage in plastic makes it possible to retain the sediment from the sampled interval of the core. This sample can still be used by sedimentologists and paleontologists.

(2) A workshop should be convened to explore methods of routine shipboard sampling and analysis of hydrocarbon gases in sediments. At this workshop various methods and modifications of methods can be considered in detail. The product expected would be a report outlining a procedure which ODP can support for development and implementation. Persons invited to attend should be those well-experienced in analyzing gases and those who will have the responsibility to develop the technology or carry out the procedure.

4. Gas Analyses

On the ship there are presently two Hewlett-Packard 5890A gas chromatographs. Operation of these instruments is described later. One has had an optional valving system (Option 820) added specifically for the analysis of natural gas mixtures. The instrument is called a Natural Gas Analyzer (NGA). At first glance, it would appear that this instrument should be ideal for shipboard hydrocarbon gas analyses. Unfortunately the NGA has some limitations:

(1) The program for analysis of C_1 through C_6 hydrocarbons now takes about 30 min, and the last compounds to elute are ethane and methane, the compounds of great interest in monitoring for safety. Such a long analysis time is not acceptable when coring in gassy sediments where the information regarding gas composition is needed quickly in order not to delay the drilling operation.

(2) The fixed sample loop is only 0.25 cc. A sample loop of 1.0 cc would increase sample size by a factor of 4 which could be important. The capability of this analysis system is less than that available on the Glomar Challenger where the gas samples were concentrated through the removal of methane before analysis.

(3) The gas chromatographic columns of the NGA are seriously affected by water. Because water vapor is present in headspace samples as well as in vacutainer samples taken from gas pockets in the cores, one can expect the columns to deteriorate with time. This problem can be solved by addition of a drying tube in the sample line. This drying tube should be changed regularly because the drying system has no means of self regeneration.

(4) At present only one detector (Flame Ionization = FID) of the NGA has an integrator attached to it. Both detectors (FID and Thermal Conductivity = TCD) should be monitored during a run. The computers do acquire the data from both

detectors, but an integrator trace is still needed for the second detector for real time interpretation and especially when the computers are down, as they were on the first part of Leg 104. Thus, an additional Hewlett-Packard 3392A Integrator should be part of the NGA system.

(5) Because the chromatographic program of the NGA is so long (30 min), another means must be found to measure at least the methane/ethane ratios in less than about 3 min. To meet this requirement on Leg 104, we installed a 12' x 1/8" Poropak Q column in the second HP 5890A gas chromatograph thus eliminating at least temporarily the use of this instrument for heavy hydrocarbon analyses. With the Poropak Q column, we were able to obtain methane/ethane ratios quickly, but at the expense of the loss of our capability to measure heavy hydrocarbons. Of course one can always switch back and forth with difficulty. But the time may come when gassy sediments as well as liquid hydrocarbons are observed in cores, and both gas and heavy hydrocarbon analyses will be required at the same time and required quickly. We believe that a small and inexpensive gas chromatograph should be purchased to measure specifically methane/ethane ratios rapidly. The Carle 800 on the Glo-mar Challenger was quite satisfactory for this purpose. A new instrument should be a small, isothermal TCD gas chromatograph with sample loop and backflush capabilities.

5. Other Considerations

Currently ODP requires that gas in gas pockets developed in cores be measured routinely. This measurement utilizes vacutainers to extract the gas sample through the core liners. There is a problem with the vacutainers in that they have a significant hydrocarbon blank. For example, we measured the hydrocarbon gases in vacutainers presently on the ship. The average amounts of methane and ethane were 130 and 6 ppm respectively. These concentrations are significant especially when compared to the concentrations of these compounds we observed, for example, at Site 642 of Leg 104, where the maximum methane concentration was 23 ppm and ethane was not detected in the headspace analysis. Vacutainers with lower hydrocarbon backgrounds need to be found.

J. Whelan at Woods Hole Oceanographic Institution has obtained satisfactory vacutainers by making her own from tubes supplied by Wheaton Company and with stoppers coated with silicone. We measured the gas composition of one of her vacutainers and found only 3 ppm methane and no detectable ethane. It may be possible to flush with helium the vacutainers presently on the ship and reestablish the vacuum. By this means we may be able to reduce the blank to acceptable levels (see Appendix B for details of vacutainer preparation).

B. ORGANIC CARBON

Organic material is a fundamental constituent of sediments, and organic carbon is a basic measure of this material. The concentrations of organic carbon play a major role in the interpretation of the productivity and preservation of organic matter in sediments and in the evaluation of potential

source rocks of petroleum. The measurement of organic carbon has been a routine part of DSDP and should be part of ODP. In DSDP, organic carbon was sometimes measured on shipboard by means of an elemental (CHN) analyzer and then routinely in the shorebased laboratory in La Jolla, California, by means of a LECO combustion system. If accurate organic carbon measurements for ODP can be made routinely on shipboard, then important data will be available for immediate use by the leg's scientific staff, and also the information can become part of the permanent, fundamental record of the cruise. Additional organic carbon values will not have to be determined in the shorebased laboratory except for special purposes.

A major question is, of course, can accurate organic carbon determinations be made on shipboard? Presently the Perkin-Elmer 240C Elemental Analyzer is the only instrument on board that is capable of providing this measurement. Our experience with this instrument has not been completely satisfactory. At best, we believe that the organic carbon values that we obtained are good "estimates" of the organic content of the sediments, but we lack confidence in the accuracy of our measurements. This lack of confidence comes from the fact that we obtained poor values for nitrogen and hydrogen. We have used the carbon values, however, because they replicate, compare well against the standards, and are in the correct range relative to results reported for sediments collected on Leg 38 which also sampled in the Norwegian Sea (Morris, 1976).

As an alternative to the Elemental Analyzer, we recommend that ODP consider the Coulometrics 5020 Total Carbon Apparatus coupled with the 5010 CO₂ Coulometer (Fig. 3). This instrument is designed specifically for total carbon and organic carbon in solids and liquids. Presently the shipboard laboratory has the Coulometrics 5030 Carbonate Carbon Apparatus and the 5010 CO₂ Coulometer, and this instrument has been shown to provide excellent measurements of carbonate carbon. Utilization of both the Carbonate Carbon Apparatus and the Total Carbon Apparatus should give very accurate assessments of the carbon content of sediments. We suggest that ODP consider adding the Total Carbon Analyzer to the shipboard equipment after evaluation and testing.

If it can be shown that the Total Carbon Analyzer can provide precise and accurate measurements of total organic carbon, then the following routine program should be adopted: for organic carbon determinations, a plug of sediment (10 cc) should be taken from the working half of the core at the time of shipboard sampling. This plug should be taken every third core and adjacent to the 30-cm interval from which the organic geochemistry (OG) sample was removed. The sample will be dried and portions used for determination of carbonate carbon and total carbon with the organic carbon being determined by difference. Alternatively, a portion of the sample can be used for the determination of carbonate carbon and another portion can be acidified, washed, and dried; organic carbon can be determined directly on this acidified material. This routine sampling and analysis will provide an estimate of the carbon content of the adjacent, large OG sample. This information will be invaluable to later investigators who will be sampling the OG sample in the future. In addition, a systematic (every third core), and accurate record of

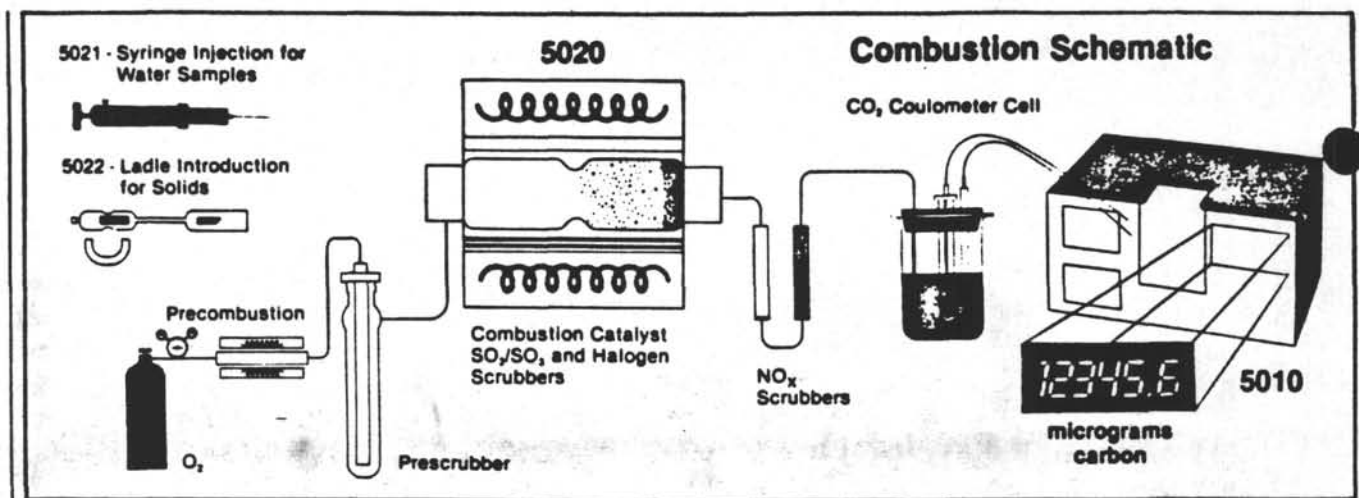


Figure 3. Total Carbon Apparatus (Coulometrics, Inc., Wheatridge, Colorado).

organic carbon will be available for every ODP hole in which sediment is cored.

C. EXTRACTABLE ORGANIC MATERIAL

During Leg 104 we did not have the opportunity to look for extractable organic material in sediments. We did, however, examine potential organic geochemical contaminants which would greatly interfere with the analyses of this material (Appendix A). In doing our work we noticed a lack of appropriate laboratory supplies. We see a need for an extraction system, a means to evaporate and concentrate small volumes of solvents, disposable chromatographic columns, and vials for sample collection and storage. We believe that these supplies should be added to the laboratory in order to provide a modest capability for the study of extractable organic material.

D. SUMMATION

We have suggested that two routine sampling and analysis procedures for organic geochemistry be adopted as part of ODP's shipboard operation. One procedure monitors hydrocarbon gases, and the other monitors organic carbon. The adoption of these procedures will require additional equipment. We believe that the routine program is important enough to justify the purchase of additional instrumentation. Although the laboratory is already crowded, there is still room for the recommended instruments with some reorganization. Future use of the laboratory may demonstrate that some of the instruments now on board can be removed. At the moment, however, it is not obvious which ones to suggest because each one yields some information of interest to organic geochemistry.

IV. INSTRUMENTATION FOR ORGANIC GEOCHEMISTRY

Very modern instrumentation is available in the chemical laboratory of the JOIDES Resolution for organic geochemistry. On Leg 104 we made use of the following instruments:

Hewlett-Packard 5890A Gas Chromatograph with Option 820 (Natural Gas Analyzer) and two detectors [flame ionization (FID) and thermal conductivity (TCD)]. For analysis of gases in sediments.

Hewlett-Packard 5890A Gas Chromatograph with both packed and capillary column capability. Both the FID and TCD can accept either packed or capillary columns. For determination of low and high molecular weight hydrocarbons.

Hewlett-Packard 3350 Laboratory Automation System (LAS).
Receives data from the gas chromatographs through A/D converters.

Chromatographic Plotting Package (CPLOT) a software program used in conjunction with IAS for integration and plotting of chromatographic data.

Rock-Eval II with TOC. For determination of source and maturity of organic matter.

Perkin-Elmer 240C Elemental Analyzer. For analysis and quantification of carbon, hydrogen, and nitrogen.

Coulometrics 5030 Carbonate Carbon Apparatus. For the accurate determination of inorganic carbon.

Dionex 2021i Ion Chromatograph. For determination of ions in pore water.

A. NATURAL GAS ANALYZER (NGA)

The NGA is a special option (Option 820) for the Hewlett Packard (H-P) 5890A gas chromatograph. The system employs three columns and appropriate automatic valve switching to provide a complete and rapid determination of oxygen, nitrogen, methane, carbon dioxide, ethane, propane, the butanes, the pentanes, and the total hexane+ (C_{6+}) hydrocarbons. The method may be changed for the separation of the C_{6+} hydrocarbons or abbreviated for the analysis of "lean" gases. We suggest, however, that the NGA be run in the standard gas analysis mode and that the other H-P 5890A gas chromatograph be used for special purposes. Table 1 describes columns and valves in the NGA. Figure 4 shows a schematic of the column systems, and Figure 5 shows a typical gas chromatograms obtained from standard mixtures of gases.

The NGA is controlled by the keyboard on the front right side of the GC. This keyboard controls the temperature settings of the ovens, detectors, and injection ports, along with the signal settings such as ranges and signal outputs. Table 2 gives a set of conditions which we found worked well. The manual located near the instrument gives details on programming the instrument, and a card located on the left side of the GC in the side door provides a quick reference to the control panel. Control of the three valves is accomplished by using the H-P 3392 Integrator. Table 3 lists the integrator parameters that we found to be adequate. The NGA is interfaced through IAS to the H-P-1000 mainframe computer. This computer accepts raw data from the GC and stores these data in a result file unique to that sample. This procedure permits different analyses of data from the same sample and provides the capability to plot the file on an H-P 7470A Plotter.

The NGA is operated as follows: A gas sample is injected on the 3 column system through a 0.25 ml sample loop. We suggest filling a 5 ml syringe with the sample and using this volume of gas to flush the loop during injection of the sample. As the last of the gas is expelled from the syringe, press the

Table 1. Description of columns and valves in the Natural Gas Analyzer.

All columns are 1/8" stainless steel.

Column #1 35% DC200 silicone oil on 80/100 mesh 6 ft.

Used to separate propane through hexane.

Column #2 80/100 mesh Porapak Q 6 ft.

Used to separate ethane and carbon dioxide.

Column #3 45/60 mesh Molecular Sieve 10 ft.

Used to separate oxygen, nitrogen, and methane.

TCD reference column is an 18 inch 10% UCW 983.

Valve #1 is a 10 port valve, including direct connection to sample loop and column 1.

Valve #2 is a 6 port valve, includes direct connection of column 2.

Valve #3 is a 6 port valve, direct connection to column 3 and TC detector.

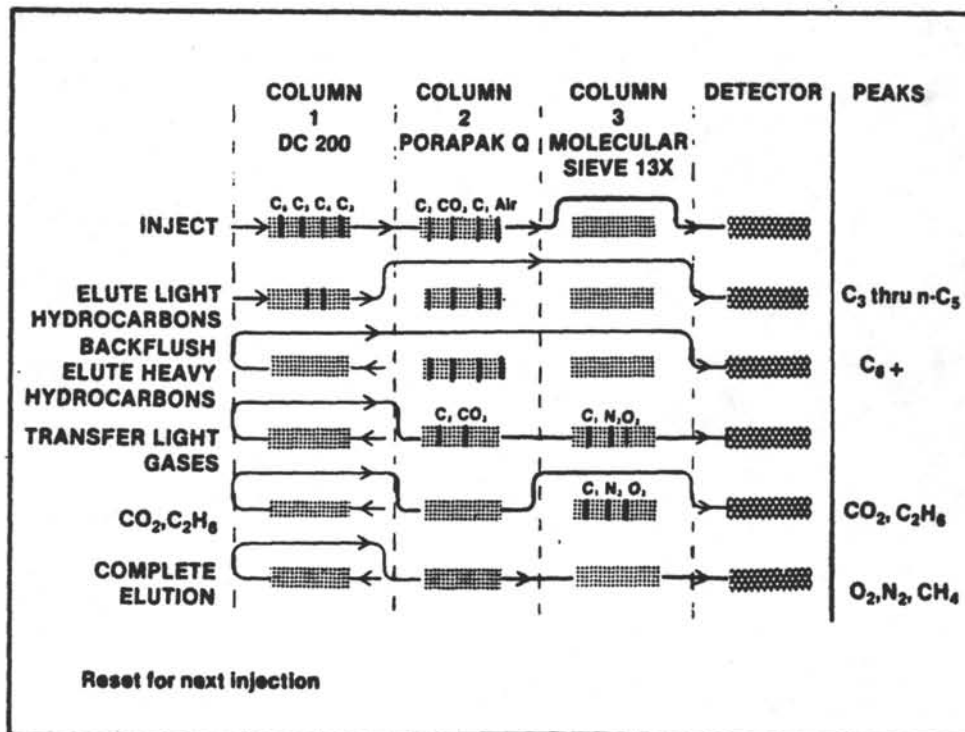


Figure 4. Schematic diagram of the column system of the Natural Gas Analyzer.

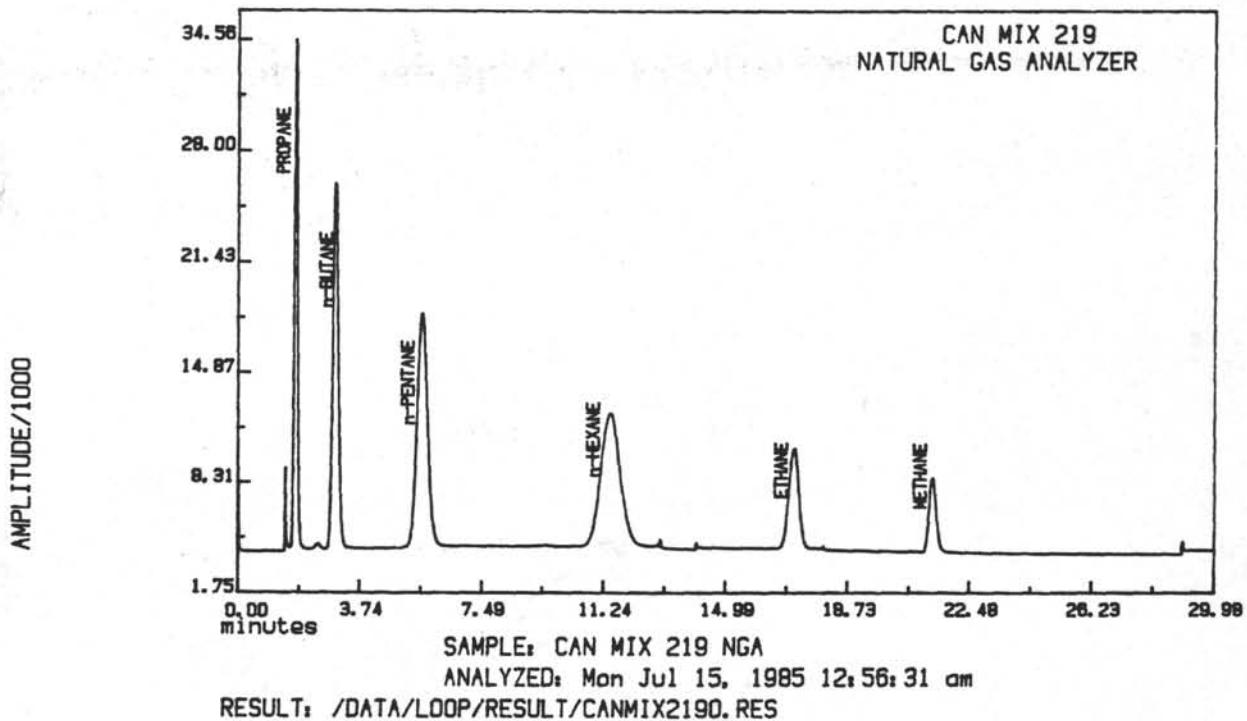
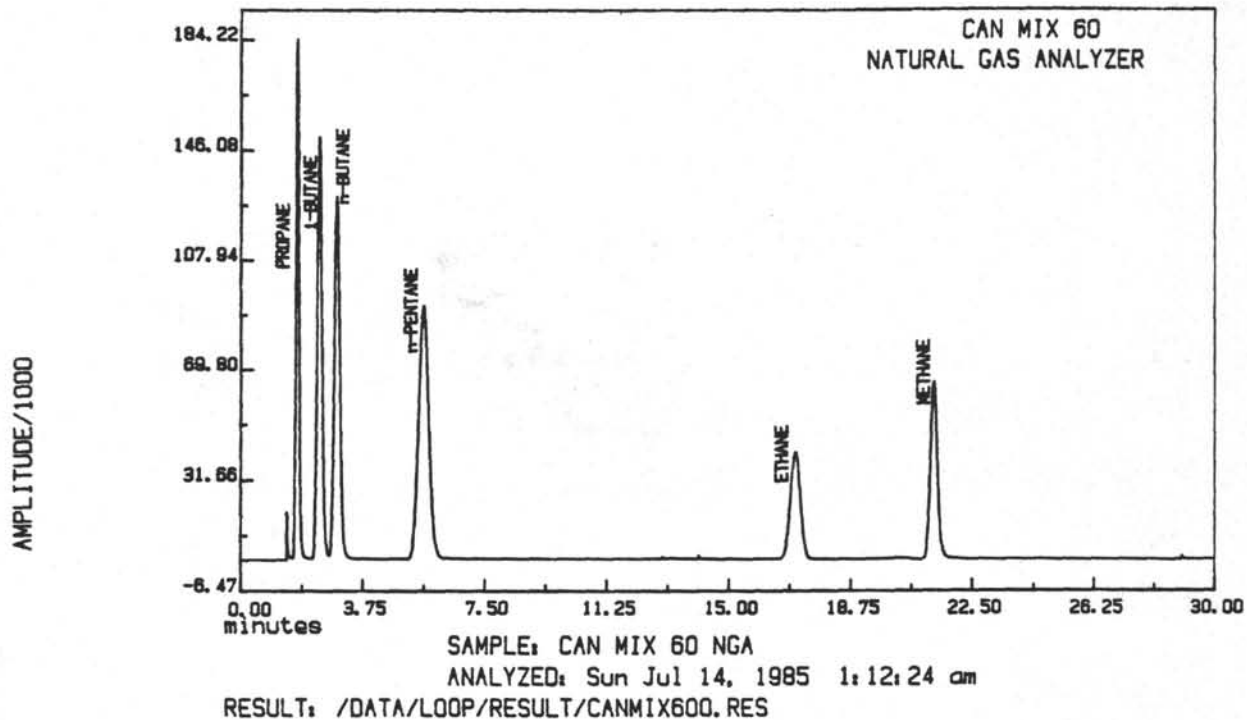


Figure 5. Gas chromatogram obtained from the Natural Gas Analyzer showing analyses of Scotty IV Can Mix 60 and 219.

Table 2. Gas chromatographic conditions for the Natural Gas Analyzer.

Air pressure	42 PSI.
Hydrogen Pressure	16 PSI.
Helium Pressure	53 PSI.
Range FID and TCD	0
Attn FID and TCD	0
Detector Temp FID	100 C.
Detector Temp TCD	100 C.
Isothermal Program.	
Oven temp	70 C.
Run time	30 min.

Table 3. Integrator parameters used for the analysis by the Natural Gas Analyzer of standard gas mixtures shown in Figure 5.

LIST: METH @

RUN PRMTRS

ZERO = 10
 ATT 2† = 7
 CHT SP = 0.4
 PK MD = 0.64
 THRSH = 2
 AR REJ = 10000

RPRT OPTNS

2. PF UNC PKS= 2.3305E-05
 3. MUL FACTOR= 1.0000E+00
 4. PK HEIGHT MODE NO
 5. EXTEND RT NO
 6. RPRT UNC PKS YES

TIME TBL

0.00 INTG # = 8
 30.00 STOP

CALIB TBL

ESTD CALIB RUNS 1
 REF % RTW= 5.00 % RTW= 5.00

CAL #	RT	AMT	AMT/AREA
1	21.25	9.4230E+01	7.9700E-05
2	17.22	9.5860E+01	4.0200E-05
3	1.74	1.0060E+02	2.8300E-05
4	2.91	1.0120E+02	2.2400E-05
5	5.50	1.0240E+02	2.0200E-05
6	11.12	9.8250E+01	1.7800E-05

LIST: EXT # TIME @

19405A SAMPLER/EVENT CONTROL MODULE
 LOOP ADDRESS: 1

EXTERNAL EVENT TABLES

NO AUTO RESET

TIME TABLE:

TIME	EXT #	STATE
0.01	7	ON
0.10	5	ON
1.40	6	ON
12.90	5	OFF
13.00	6	OFF
13.00	7	OFF
14.10	7	ON
19.00	7	OFF
29.00	6	ON
29.00	7	ON
30.00	6	OFF
30.00	7	OFF

start button on the integrator; this action starts the GC and the integrator. Quickly press the start button on the appropriate A/D converter. By following Tables 2 and 3 and Figure 4 one can trace the flow of sample through the different columns and valves.

Comments:

- 1) Because of extensive valve switching one must be careful that a component is completely through a valve before the valve is turned off or carry over will occur.
- 2) To monitor both channels on the computer, both A/D converters must be started, and each one must have a unique file name.
- 3) The computer and integrator will give different areas for the same peak (consistent within themselves); therefore, the same response factor cannot be used for both systems. Use both methods as a check. Calculate response factors at least twice a week or more if helium tanks, columns, etc. are changed.
- 4) Be careful not to inject water onto the columns because water will destroy the Porapak packing.
- 5) If any conditions, settings, etc on either the GC, integrator, or computer are changed, document these changes very carefully.
- 6) Change the septum about every 15 injections even though it is in a sample loop because there is a particle filter in-line, and some back pressure is created during injection into the sample loop.

B. HEWLETT-PACKARD 5890A GAS CHROMATOGRAPH

This instrument provides numerous choices among inlets, columns, and detectors through inlet lines and adapters. Packed or capillary columns can be used without sacrificing performance. This instrument is mainly for high-resolution gas chromatography. There are two detectors, flame ionization (FID) and thermal conductivity (TCD), and two inlet ports. Either detector can be used with packed or capillary columns.

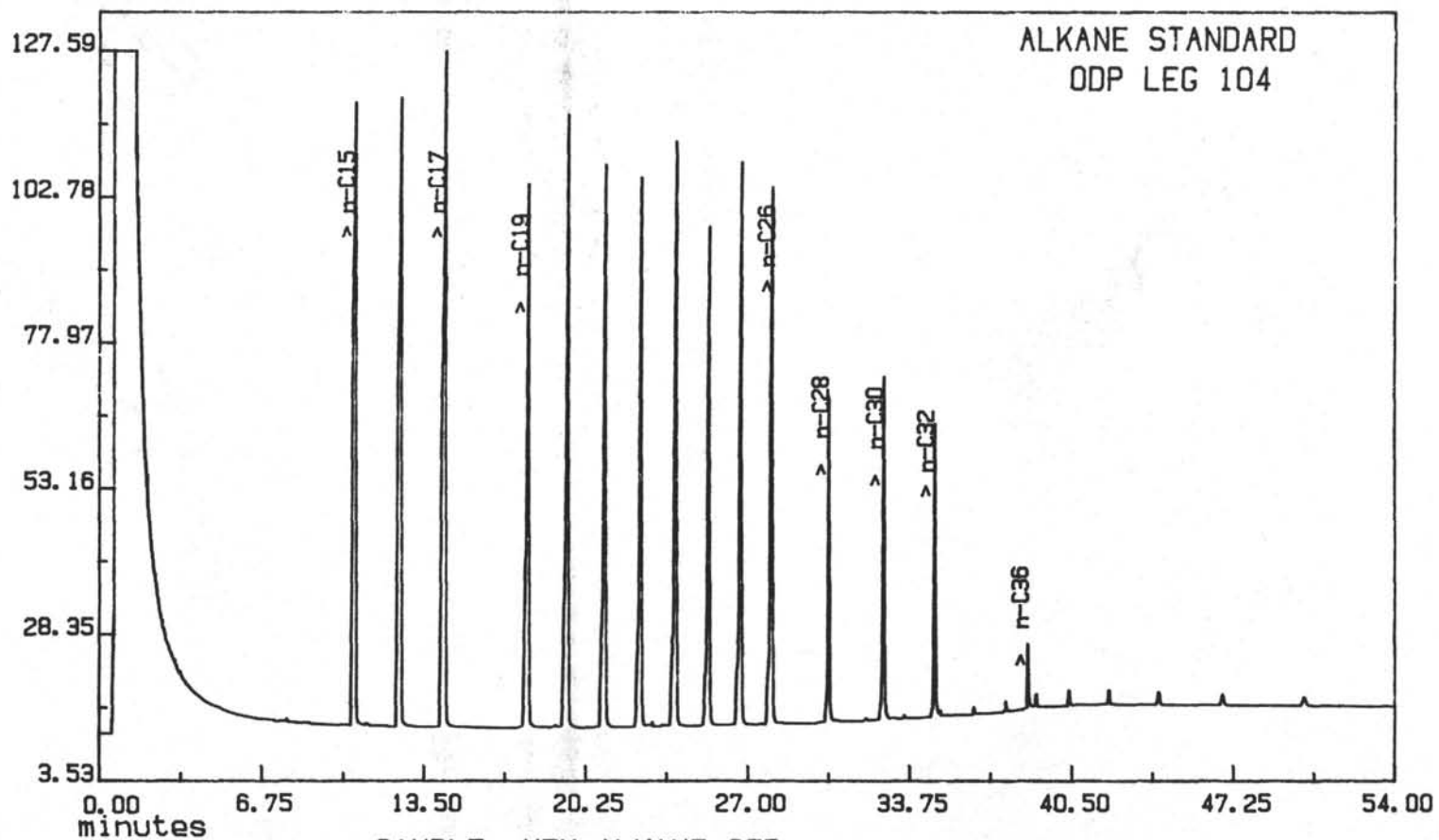
On Leg 104, this instrument was used in both the packed and capillary column modes. Methane/ethane ratios can be determined by means of 1/8" X 9' or 12' Porapak Q or molecular sieve, packed columns on the TCD. A typical injection volume is 0.2 ml of gas, or less if concentrations become high. Gas chromatographic peaks are integrated on an H-P 3392 integrator and on IAS.

The high-resolution capillary capability permits real-time evaluation of heavy hydrocarbons. The columns available on the ship are H-P Ultra performance capillary columns (0.20mm internal diameter) coated with a 0.11 thickness of cross linked methyl silicone. A typical injection volume is 1 microliter. An example chromatogram (FID) of a standard mixture is shown in Figure 6. Chromatographic peaks are integrated as above. The GC conditions for this analysis are shown in Table 4.

Comments:

- 1) Helium is the appropriate carrier gas for this instrument. Hydrogen should never be used as the carrier gas for the capillary column. Resolution is not enhanced sufficiently to warrant the safety hazard on the ship.
- 2) The capillary column should not be overloaded. These columns are designed for low loads and high efficiency. The computer can always enhance the signal.
- 3) Porapak will melt above 250°C. The column with that packing must be removed when the capillary system is in use, and the oven temperature taken to limits beyond 180°C. Condition the Porapak columns at 180°C.
- 4) Change the septum every 10 samples, particularly when the injection port is at 300°C.
- 5) When the various zones are heated always have the carrier, reference, and auxillary gases flowing through the system.
- 6) Oxygen will destroy the filament in the TCD. Turn off this detector when not in use or when the helium flow will be interrupted. These detectors take only about 1 minute to equilibrate.
- 7) When using the FID make sure the proper jet is in the collector assembly. There are different jets for packed and capillary columns.
- 8) The position of the capillary column in the injection zone is extremely important. The column must be 4 cm beyond the edge of the column nut on the detector side and 0.6 cm on the inlet side. Check the manual on how to measure these distances.
- 9) Be sure the glass inlet sleeve for the capillary column is not cracked and that it is positioned so the top is flush with the injection port and the o-ring is placed properly. A diagram is in the manual.

AMPLITUDE/1000 (Enlarged x 4.0)



SAMPLE: NEW ALKANE STD
ANALYZED: Sun Jul 14, 1985 1:13:23 am
RESULT: /DATA/LOOP/RESULT/STANDARD2.RES

Figure 6. Gas chromatogram obtained by capillary chromatography showing an analysis of a standard mixture of n-alkanes ranging from n-C₁₅ to n-C₃₆.

Table 4. Gas chromatographic conditions and integrator parameters used for the analysis by capillary chromatography of the n-alkane standard shown in Figure 6.

Air	400 ml/min
Hydrogen	33 ml/min
Carrier Helium	4 ml/min
Aux Helium	28 ml/min
Range 0	
Attn 0	
splitless mode	
Injection temperature	300 C.
Detector temperature	300 C.
Temperature 1	40 C.
Time 1	1 min.
Rate 1 C/min	30 C.
Final temperature 1	80 C.
Final time 1	0 min.
Rate 2 C/min	6 C.
Final temperature 2	300 C.
Final time 2	15 min.

LIST: METH @

RUN PRMTRS

ZERO = 10
 ATT 2† = 8
 CHT SP = 0.4
 PK WD = 0.04
 THRS = 3
 AR REJ = 100000

RPRT OPTNS

2. RF UNC PKS=	0.0000E+00
3. MUL FACTOR=	1.0000E+00
4. PK HEIGHT MODE	NO
5. EXTEND RT	NO
6. RPRT UNC PKS	NO

TIME TBL

0.01 INTG #	= 9
0.03 INTG #	= 8
0.05 INTG #	= 7
7.00 INTG #	= -9

C. LABORATORY AUTOMATION SYSTEM (LAS)

LAS is the software system that accepts digital data from the gas chromatographs and ion chromatographs. This system has been designed to help process the generated data into both tables and chromatographic plots. The software is used in a screen dialog mode; the user controls the program with a pointer and 8 soft keys. LAS stores the acquired digitized data from each chromatographic run in a unique result file as designated by the operator. Methods are set up to analyze the raw data; these methods are used to name peaks, to determine concentrations based on areas of individual peaks, to calculate total sample concentration, and to store this information in a processed file which can be used in CPLOT.

Comments:

- 1) LAS is a very powerful program that is easy to operate and should be used to its fullest extent.
- 2) It is probably best to operate LAS in the pause mode rather than in autotime.
- 3) Files must be unlocked from the A/D converter before they can be reanalyzed.
- 4) Methods need to be updated regularly especially with regard to the response factors.

D. CHROMATOGRAPHIC PLOTTING PROGRAM (CPLOT)

CPLOT is a comprehensive chromatogram plotting program for use with the LAS system. CPLOT allows the manipulation of the collected data to enhance or suppress the signal, to analyze a chosen time window, and to calculate area. CPLOT is controlled through 8 soft keys, 3 main menus, and 10 speciality menus. Only LAS result files and method files may be used in CPLOT. With this system raw data is never lost, and it can be plotted in numerous ways. Figures 5 and 6 were generated utilizing CPLOT.

Comments:

- 1) Publication quality chromatograms can be generated with CPLOT and the H-P 7470A Plotter.
- 2) CPLOT is user friendly.

E. ROCK-EVAL II WITH TOC

Rock-Eval is a whole rock or sediment pyrolysis system used to ascertain the type and maturity of organic matter and to estimate petroleum potential.

The pyrolysis technique involves a microprocessor controlled temperature program that causes the release of the light-end hydrocarbons, recorded as a peak called S1, and the thermal cracking of the kerogen matrix producing peak S2. During the pyrolysis of the sediment/rock, CO₂, produced from the organic matter, is indicated as peak S3, and is trapped only between the initial starting temperature and 390°C; this trapping avoids other sources of CO₂, such as carbonate, especially siderite which is the most labile carbonate (Tissot and Welte, 1984). A fourth parameter is T_{max} which is the pyrolysis temperature at which the S2 peak reaches a maximum. Finally the total organic carbon (TOC) is measured. Rock-Eval automatically prints the results as a pyrogram (Fig. 7), in a data table, and in a bar graph.

The five basic parameters (S1, S2, S3, T_{max}, TOC) are used to calculate, productivity index (PI), petroleum potential (PC), hydrogen index (HI), and oxygen index (OI). Tissot and Welte (1984) discuss Rock-Eval on pages 509-518. Productivity index (PI) is defined as S2/(S1+S2); values of PI (mgHC/g rock) generally increase with depth and can also be used to pinpoint zones of unusually high or low amounts of hydrocarbons. Petroleum potential (PC) is defined as [k(S1+S2)] where k=0.08. PC is also known as pyrolyzed carbon and represents the maximum quantity of hydrocarbons which can be produced from the source sediment or rock given sufficient burial depth and time. PC is expressed in mgHC/g rock. Hydrogen index and oxygen index are used in kerogen classification and are calculated as follows:

$$\begin{aligned} \text{HI (mgHC/g organic C)} &= 100(\text{S2})/\text{TOC} \\ \text{OI (mgCO}_2\text{/g organic C)} &= 100(\text{S3})/\text{TOC} \end{aligned}$$

Table 5 and Figure 8 aid in interpretation of the data and in classification of the kerogen into the appropriate maturity levels and types.

Comments:

- 1) Reproducibility of S1, S2, S3, T_{max} is very good.
- 2) TOC values at present (July 1985) are unreliable.
- 3) Because of the time required for sample preparation, the instrument is limited as a real time interpretive tool for safety considerations.
- 4) Rock-Eval data can easily be overinterpreted and, therefore, should be treated conservatively.
- 5) Approximately the same quantity of sediment should be analyzed for a given group of samples.
- 6) Samples should not be run until the blanks are very low.

DATE: 07-11-85

STANDARD

CYCLE : 1

SCALE = 1/32

OTHER STD : S2= 5.64 S3= 0.89 S4 = 14.48 TMAX = 420
STD-QTY = 99.0 S 1 = 00001320 S 2 = 00023646 S 3 = 00005209 TMAX = 413

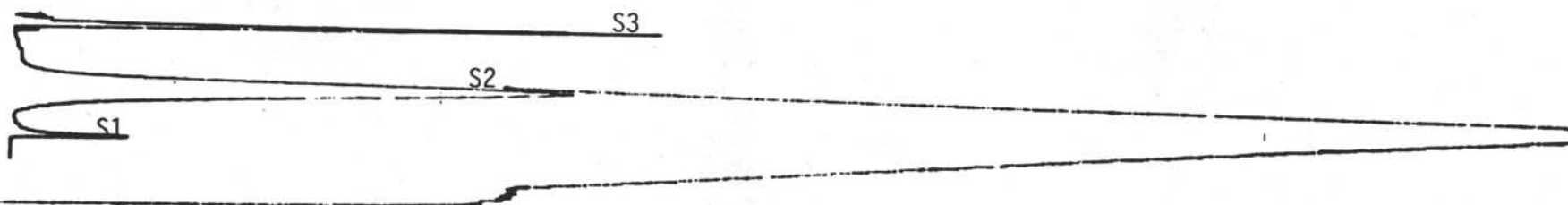


Figure 7. Rock-Eval pyrogram showing the results of analysis of a standard rock sample (Delsi Standard).

Table 5. Guidelines for the interpretation of Rock-Eval data.

Petroleum Potential (PC values)

80% Type I Kerogen
50% Type II Kerogen
10-15% Type III Kerogen

S2/S3 values.

0-2.5 gas and Type III
2.5-5.0 oil and Type III
5-10 oil and Type I and II

Maturity Tmax

0-435 C. immature
435-450 C. oil zone
450-470 C. gas zone

HI and OI plotted on Van Krevelen type diagram.

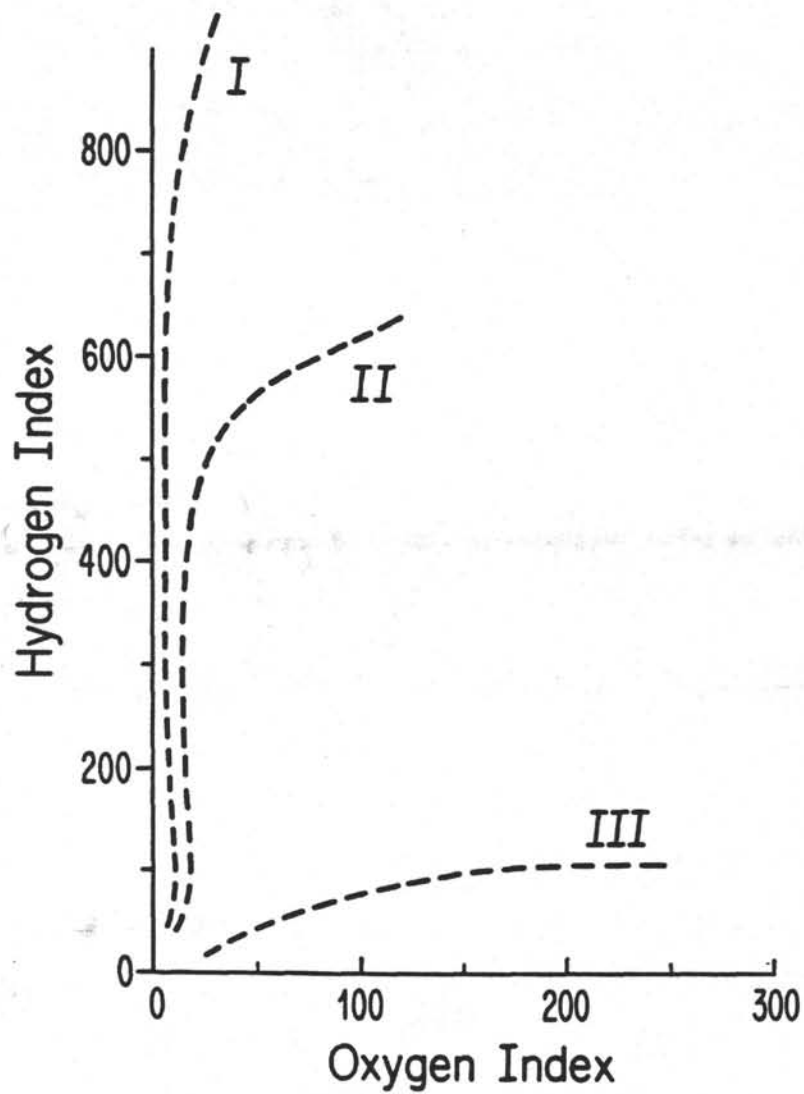


Figure 8. Van Krevelen-type diagram for the classification of source rock types by means of hydrogen and oxygen indices.

F. PERKIN ELMER 240C ELEMENTAL ANALYZER

The elemental analyzer is used in organic geochemistry to determine the carbon, hydrogen, and nitrogen content of organic compounds in sediments. Combustion of the sediment occurs in a pure oxygen environment under static conditions. The combustion products are analyzed automatically in a self-integrating, steady state thermal conductivity detector. Results are recorded with a Perkin-Elmer Data Station which analyzes the data and stores it permanently.

There are three main components in the elemental analyzer: combustion train, analytical system, and the electronics package. The combustion train includes the combustion and reduction furnaces. In the analytical system are the detector, mixing chambers, and the gas traps. The electronics package includes the temperature controls and the data station. The elemental analyzer requires a 1-3 mg sample of sediment in a platinum boat of which an accurate weight is known; analysis time takes 12 minutes.

Comments:

- 1) Accurate weighings are extremely important and difficult to make at sea.
- 2) Blank values must be low for all three parameters (C,H,N).
- 3) Sediment samples must be homogeneous.
- 4) Caution must be exercised when reporting the hydrogen and nitrogen values. We were unable to obtain reliable results for these elements.
- 5) Each sample should be run 2 or 3 times to check reproducibility.

G. COULOMETRICS 5030 CARBONATE CARBON APPARATUS

The Coulometrics carbon analyzer rapidly and accurately determines CO_2 from a variety of sources. The Coulometrics Model 5010 CO_2 Coulometer, which is the detector for the Carbonate Carbon Apparatus, is filled with ethanolamine and an indicator. When gas is passed through the solution, CO_2 is quantitatively absorbed and is converted to a strong acid by the ethanolamine. The coulometer electrically generates a base to return the indicator color to the starting color. Results are given in micrograms of carbon and percent CaCO_3 . CO_2 is generated by treatment of the sediment with HCl and gentle heating; the evolved CO_2 is transferred to the coulometer by a purified air stream. Analysis time is 3 to 7 min.

Comments:

- 1) The instrument is very sensitive, and results are reproducible.
- 2) Accurate weights of sediment samples are needed to ensure precise measurements. Sample size depends on the content of carbonate carbon which should be in the range of 1 to 5 mg. Typically we used 250 mg of sediment.
- 3) The coulometer solution should be changed about every 10 samples and more often in high carbonate areas to ensure that CO_2 is completely absorbed.
- 4) Grease the joints on the sample tubes each time to prevent CO_2 loss.
- 5) Sample tubes need to be completely dry so that when sediment is added it will not adhere to the walls above the acid inlet point.

H. DIONEX 2021I ION CHROMATOGRAPH

The ion chromatograph is an automated liquid chromatographic system using ion exchange mechanisms and suppressed conductivity detection for the separation and determination of anions and cations. The ion chromatograph consists of four basic parts: sample delivery, columns, detectors, and integrators.

Comments:

- 1) Although this instrument is used mainly for inorganic geochemistry, it does quantify sulfate and chloride which may be of interest to organic geochemists.
- 2) For sulfate analyses we found it necessary to clean the column between each sample with an injection of distilled water.
- 3) The detector should return to the initial conductivity reading before the next sample is injected.
- 4) The LAS system helps quantify chromatographic peaks.
- 5) Fresh eluent and regenerate should be used often.

V. CONCLUSIONS

The important point of this report is the recommendation that ODP establish a routine monitoring program for organic geochemistry. The program should include (1) regular sampling (at least every 30 m of core), and (2) analyses of collected samples for hydrocarbon gases and organic carbon. To begin with, the hydrocarbon gases should be analyzed by the headspace technique until a better procedure is devised. The routine organic carbon measurements should start as soon as a method is proven which provides accurate and precise determinations at sea. Possible approaches to carrying out the recommended organic geochemical program are described in detail. These approaches include (1) organizing a workshop to attempt to design an optimum method for analyzing hydrocarbon gases in sediments, and (2) purchasing and evaluating a Total Carbon Apparatus for the specific determination of organic carbon in sediments.

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APPENDIX A: Catalogue of Potential Organic Geochemical Contaminants[†]

Introduction

At least thirty-five different organic and organic-related substances in use aboard the JOIDES Resolution (SEDCO/BP 471) can become incorporated in cores during the sampling procedure. For the most part, these contaminants do not interfere with scientific studies of the core material; however, certain investigations in organic geochemistry can be seriously affected by the presence of these substances. For example, naturally occurring bitumen is of special importance to petroleum geochemists. Bitumen, also called extractable organic material (EOM), is recovered from sediments by solvent extraction, but the contaminants that have found their way into the cores will also be extracted by the solvent. Therefore, in the analysis of bitumen in oceanic sediment collected through the Ocean Drilling Program (ODP), it is essential that distinction be made between naturally occurring bitumen and organic contaminants. The purpose of this catalogue is to provide a guide to shipboard substances that can contaminate cores and become a potential problem for organic geochemistry.

The collection and analysis of potential organic geochemical contaminants was begun on ODP Leg 103 (Dunham, in press). Nine substances were identified and analyzed by gas chromatography. We have now assembled a collection of 35 potential organic geochemical contaminants. The following information is provided for each of these materials: common or trade name, product description, manufacturer, and general usage during drilling, coring, and laboratory operations. The substances have been organized into four groups according to the probability of the material contaminating the core; the groups range from those materials with high probabilities of being contaminants to those that have very little chance of getting into the cores.

Each of the 35 substances was placed in hexane; most of the substances dissolved in this solvent, but some only partially went into solution. The mixtures were analyzed by gas chromatography, and the resulting chromatograms are "fingerprints" of 35 potential organic geochemical contaminants. These chromatograms form the basis of this catalogue.

Methods

For this work, 60 to 100 mg of each substance were weighed on a Scientech 202 Electronic Balance in glass vials. Each sample was dissolved in 5 ml of

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HPLC-Grade, n-hexane (Baker Analyzed Reagent). Of the resulting mixture, one microliter (lesser amounts for specific materials) was analyzed by high-resolution, capillary, gas chromatography (H-P 5890A Gas Chromatograph). The results were reported through an H-P 3392 Integrator and the LAS-CPLOT computer system. Conditions for gas chromatography under which all samples were run are given in Table A-1. Figure A-1 shows a gas chromatogram of a standard n-alkane mixture, prepared onboard from kits (Poly Science Corporation), with compounds ranging from n-C₁₅ to n-C₃₆. Figure A-2 is a gas chromatogram of the hexane blank which shows the background that must be present in the gas chromatograms of the samples reported here.

Results and Discussion

Descriptions of the 35 potential organic geochemical contaminants, along with the quantity of each that was placed in hexane, appear on Tables A-2, A-3, A-4, and A-5, which list, respectively, the substances having high, medium, low, and very low probabilities of contaminating the cores. Chromatographic "fingerprints", as obtained through the LAS-CPLOT computer system, are shown in Figures A-3 through A-37. These chromatograms were prepared using the same enlargement factor (3.0) in order to facilitate comparison of the various "fingerprints". The figures are arranged in the order given on Tables A-2 through A-5. Compounds in the standard (Fig. A-1) will be used for discussion of some of the "fingerprints" of the potential contaminants (Figs. A-3 to A-37).

Eleven substances with the greatest opportunity to be core contaminants are listed in Table A-2 (Figs. A-3 to A-13). Of these materials, two kinds of Pipe Dope (lead and zinc based), Line Tar, and Cable Coating are likely to get into the core during the actual drilling process. The two types of Pipe Dope, used on drill pipe and drill collar connections, are manifest chromatographically as unresolved, complex mixtures spanning a broad range of molecular weights (Figs. A-3 and A-4). Line Tar, with which the manufacturers coated sandlines and logging lines, also contains a complex mixture with discrete compounds in the range from n-C₁₅ to n-C₃₇ (Fig. A-5). The typical Cable Coating, which is sprayed on sandlines and logging lines, is composed mainly of compounds with retention times less than n-C₁₃ but also has a complex mixture of high molecular weight compounds (Fig. A-6). 3-in-One Oil, a rust inhibitor (Fig. A-7), and Parker O-Lube, an O-ring grease (Fig. A-8), both contain unresolved complex mixtures of compounds spanning different molecular weight ranges with Parker O-Lube having heavier compounds. The Silicone O-ring Grease (Fig. A-9) and the Marking Pencil (Fig. A-10) contain high molecular weight silicone compounds which extracted into the hexane solvent. WD-40 (Fig. A-11) could be particularly troublesome for organic geochemistry because it contains discrete compounds of both low and intermediate molecular weights and is used generously on the coring equipment and in the laboratory. GO-JO Hand Cleaner (Fig. A-12) has mainly low molecular weight components. Core liners are often coated with this material to aid insertion through the O-ring seals and into the core barrel; therefore, GO-JO can easily get into the cores. Also GO-JO is commonly used as a hand cleaner and thus could be transferred to cores that have been touched with bare hands. Super Agitene (Fig. A-13), from the parts cleaning tank, contains mainly low molecular weight compounds with retention times less than n-C₁₃.

Nine substances were identified which have a medium probability of contaminating the cores (Table A-3). Many of these materials are thread lubricants. Multi-grease (Fig. A-14), Jet Lube (Fig. A-15), Lubriplate (Fig. A-16), Never-Seez (Fig. A-17), Aqua Lube (Fig. A-18), and All Purpose Lube Oil (Fig. A-19) are composed mostly of unresolvable, complex mixtures of compounds having wide ranges of molecular weights. E-Z Break contains discrete compounds with retention times near $n-C_{26}$ (Fig. A-20). The chromatogram of the Compensator Oil shows a number of resolved compounds (Fig. A-21), and 7-11 Oil (Fig. A-22) is made up of mainly low molecular weight compounds with retention times less than $n-C_{13}$ but also contains some heavier molecular weight components.

Eleven substances have a low probability of being incorporated into the cores (Table A-4). Hydraulic Fluid (Fig. A-23) and Molylube (Fig. A-24) are composed mainly of complex mixtures of compounds most of which are not resolved by gas chromatography. Chromatograms of Tapeze (Fig. A-25), Rig Wash Detergent (Fig. A-26), and CO Contact Cleaner (Fig. A-27) are simple and are similar to the chromatogram of the hexane blank (Fig. A-2); these substances should pose few problems for organic geochemistry. Baker-Lok (Fig. A-28), Silicone Lubricant #111 (Fig. A-29), and Vaseline Hand Lotion (Fig. A-30) also produce simple chromatograms with a few well resolved peaks. The chromatogram for Contact Cleaner #2-26 (Fig. A-31) is much more complicated than that of the CO Contact Cleaner (Fig. A-27). The #2-26 Cleaner is composed of low and intermediate weight compounds whereas the CO Contact Cleaner apparently contains only compounds that elute with the hexane solvent. Diesel Fuel #2 (Fig. A-32) is dominated by a mixture of n -alkanes ranging up to about $n-C_{28}$, and Liquid Wrench (Fig. A-33) appears to contain n -alkanes up to about $n-C_{21}$ among other compounds.

Table A-5 lists four substances which have a very low probability of contaminating the cores. Gear Oil (Fig. A-34) contains an unresolved, complex mixture of compounds with retention times greater than about $n-C_{25}$. Carboline Thinner #10 (Fig. A-35) appears to be a simple mixture of compounds with molecular weights near that of the solvent hexane. RTV Silicone Rubber (Fig. A-36) is composed of a series of silicone compounds spanning a broad molecular weight range. Finally, the Martin Decker Fluid (Fig. A-37) is made of a complex mixture of components with retention times less than about $n-C_{17}$.

The substances having high and medium probabilities of contaminating the cores are grouped on Table A-6 according to three categories of usage: drilling, core equipment, and laboratory. Those substances used in drilling are inadvertently incorporated into the core, and this kind of contamination cannot readily be controlled. Some control can be exercised, however, in the preparation of coring equipment, but because lubrication of these parts is necessary, contamination of the core by lubricants is always a possibility. In the laboratory, careful practice and attention to detail can minimize the contamination occurring there. One possible path of contamination goes from the roughnecks' gloves to the core liner to the marine technicians' hands to the core itself.

The chromatographic "fingerprints" shown in Figures A-3 through A-37 should be useful in distinguishing shipboard-related, petroleum-like substances from

naturally occurring, petroleum-related materials that may be encountered during core recovery and processing. The conditions under which these 35 potential contaminants were prepared and analyzed have been described explicitly so that unknown samples can be analyzed in the same manner. The chromatograms in this catalogue have been reproduced at the same size as obtained from the H-P 7470A Plotter to facilitate the process of comparison of unknowns against the substances in the catalogue. The shipboard copy of this catalogue has been spirally bound so that additional chromatograms can easily be added as other potential contaminants are identified and analyzed. This catalogue should be helpful in safety monitoring and should provide organic geochemists with a preliminary means of detecting contaminated samples during cruise and post-cruise studies.

Table A-1. Gas chromatographic conditions.

Instrument:

Range = 0
Attenuation = 0
Injector Temperature = 300 C.
Detector(FID) Temperature = 300 C.
Injection mode: Splitless
Purge B on after 0.8 min.

Column:

H-P Ultraperformance capillary
Phase: Cross-linked methyl silicone
Thickness: 0.11 microns
Internal Diameter: 0.20 mm
Length: 25 m
Column Pressure: 30 psi (Helium)
Temperatures:
Initial: 40 C, 1 min.
30 C/min to 80 C.
Intermediate: 80 C
6 C/min to 300 C.
Final: 300 C, 15 min.

Table A-2. Substances with a high probability of contaminating cores.

Common/Trade Name	Product Description	Manufacturer	Usage	Wt(mg)
Pipe Dope, Lead Based (Fig. A-3)	Drill Collar Compound SEDCO L-60, 60% Lead (Pb) 293-W-7258	SEFCO, Inc. Dallas, Texas	Drill Collar and BHA connections	80
Pipe Dope, Zinc Based (Fig. A-4)	Drill Collar Compound SEDCO ZN-50, 50% Zinc (Zn) 293-R-1226	SEFCO, Inc. Dallas, Texas	Drill pipe connections	70
Line Tar (Fig. A-5)	Unknown	Greening Donald Ltd. Rochester Corporation Victor Cable Company	Coating on sand lines and logging lines. Applied during manuf.	50
Cable Coating (Fig. A-6)	CCX-77	Certified Laboratories Division of NCH Fort Worth, Texas	Sprayed on sandlines and logging lines to inhibit corrosion	50
3-in-One Oil (Fig. A-7)	Household Oil Spray	Boyle-Midway, Inc. New York, New York	Rust inhibitor on "Super Saw"	100
Parker O-Lube (Fig. A-8)	Barium Base, O-ring grease	Parker Seal Company	Greasing O-rings and seals on coring equipment	70
Silicone O-ring Grease (Fig. A-9)	Dow Corning 4-Compound	Dow Corning Corporation Midland, Michigan	Greasing O-rings and seals on coring equipment	70
Marking Pencil (Fig. A-10)	'Phano' China Marking Pencil	Joseph Dixon Crucible Co. Writing Products Div. Jersey City, New Jersey	Marking bottom of hard rock cores	50
WD-40 (Fig. A-11)	WD-40	WD-40 Company San Diego, California	Loosen rusted threads on coring and lab. equipment including "Super Saw" blades	80
GO-JO Hand Cleaner (Fig. A-12)	GO-JO Stock #1111	GO-JO Industries, Inc. Akron, Ohio	Hand Cleaning and for greasing APC core liners during insertion	70
Super Agitene (Fig. A-13)	Parts Cleaning Fluid Super Agitene M-5005-5	Graymills Corporation Chicago, Illinois	Parts cleaning tank in the tool room	60

Table A-3. Substances with a medium probability of contaminating cores.

Common/Trade Name	Product Description	Manufacturer	Usage	Wt(mg)
Multi-Grease (Fig. A-14)	Energrease BP LS EP 2	City Wide Petroleum Houston, Texas	Greasing rig equipment and core barrel swivels	60
Jet Lube (Fig. A-15)	SS-30 Jet Lube	Jet Lube, Inc. Houston, Texas	Thread corrosion inhibitor on some laboratory equipment	70
Lubriplate (Fig. A-16)	Lubriplate 630-2 PN 07201	Fiske Brothers Refining Co Lubriplate Division Newark, New Jersey	Thread lubricant on coring equipment and special tools	80
Never-Seez (Fig. A-17)	Anti-seize and Lubricating Compound, Pure Nickel Special	Never-Seez Compound Corp. Bostik Chemical Group Broadville, Illinois	Thread lubricant on coring equipment	80
Aqua Lube (Fig. A-18)	Aqua Lube	Far Best Corporation Allube Division Los Angeles, California	Water resistant lubricant for lab. equipment	60
All Purpose Lube Oil (Fig. A-19)	All Purpose Lubricating Oil	Watsco, Inc. Hialeah, Florida	Lubricating of saw on core cutter	60
E-Z Break (Fig. A-20)	High Temperature, Anti- seize and Lubricating compound	Markal Co./ Lake Chemical Company Chicago, Illinois	Thread lubricant on coring equipment	70
Compensator Oil (Fig. A-21)	Quintolubric 822-TCF Synthetic Lubricant	Quaker Chemicals	Hydraulic Oil used in motion compensator	50
7-11 Oil (Fig. A-22)	#711-B Penetrant- Lubricant	Sprayon Products Inc. Industrial Supply Division Bedford Heights, Ohio	Corrosion inhibitor containing petroleum distillates for cleaning coring parts	60

Table A-4. Substances with a low probability of contaminating cores.

Common/Trade Name	Product Description	Manufacturer	Usage	Wt(mg)
Hydraulic Fluid (Fig. A-23)	Mineral Based Hydraulic Oil, HLP-32	British Petroleum	Piperacker and most rig hydraulic systems	50
Molyube (Fig. A-24)	Molyube Grease Lithium base, 10% MoS ₂ with EP Additives	Texaco, Inc.	Iron Roughneck and other rig equipment	70
Tapeze (Fig. A-25)	Cutting Fluid Contains Trichloroethane but not Carbon Tetrachloride	Le Dez Industries, Inc. Gonzales, California	Tapping threads in machine shop	80
Rig Wash Detergent (Fig. A-26)	SEDCO Rig Wash and Laundry Detergent PN SCN008101	SEDCO, Inc. Jacintoport Facility Channel View, Texas	Washing rig floor, decks, drilling equipment	50
CO Contact Cleaner (Fig. A-27)	CO Contact Cleaner #02016	CRC Chemicals U.S.A. Warminster, Pennsylvania	Precision electronic cleaning solvent used occasionally to loosen rusted coring parts	80
Bakerlok (Fig. A-28)	Thread Locking Compound PN 199-50 Formula 'C'	Baker Oil Tools, Inc. Houston, Texas	Lock thread connections on coring parts, tools, etc.	60
Silicone Lubricant #111 (Fig. A-29)	Heavy Consistency #111 Compound	Dow Chemical Corporation Midland, Michigan	Occasional lubricant on coring and other drilling equipment	70
Vaseline Intensive Care Lotion (Fig. A-30)	Vaseline Intensive Care Hand Lotion	Chesebrough-Ponds, Inc. Greenwich, Connecticut	Hand lotion in tool room and chemical laboratory	90
Contact Cleaner (Fig. A-31)	Contact Cleaner Electrical Grade 2-26	CRC Chemicals U.S.A. Warminster, Pennsylvania	Electronic cleaning solvent used occasionally to loosen rusted coring parts	60
Diesel Fuel #2 (Fig. A-32)	Marine Gas Oil/#2 Diesel, Cetane #50	Variable suppliers	Storing core equipment if 7-11 oil is not available	50
Liquid Wrench (Fig. A-33)	PN L1-16	Radiator Speciality Co. Charlotte, North Carolina	Penetrant for freeing rusted parts on coring equipment	50

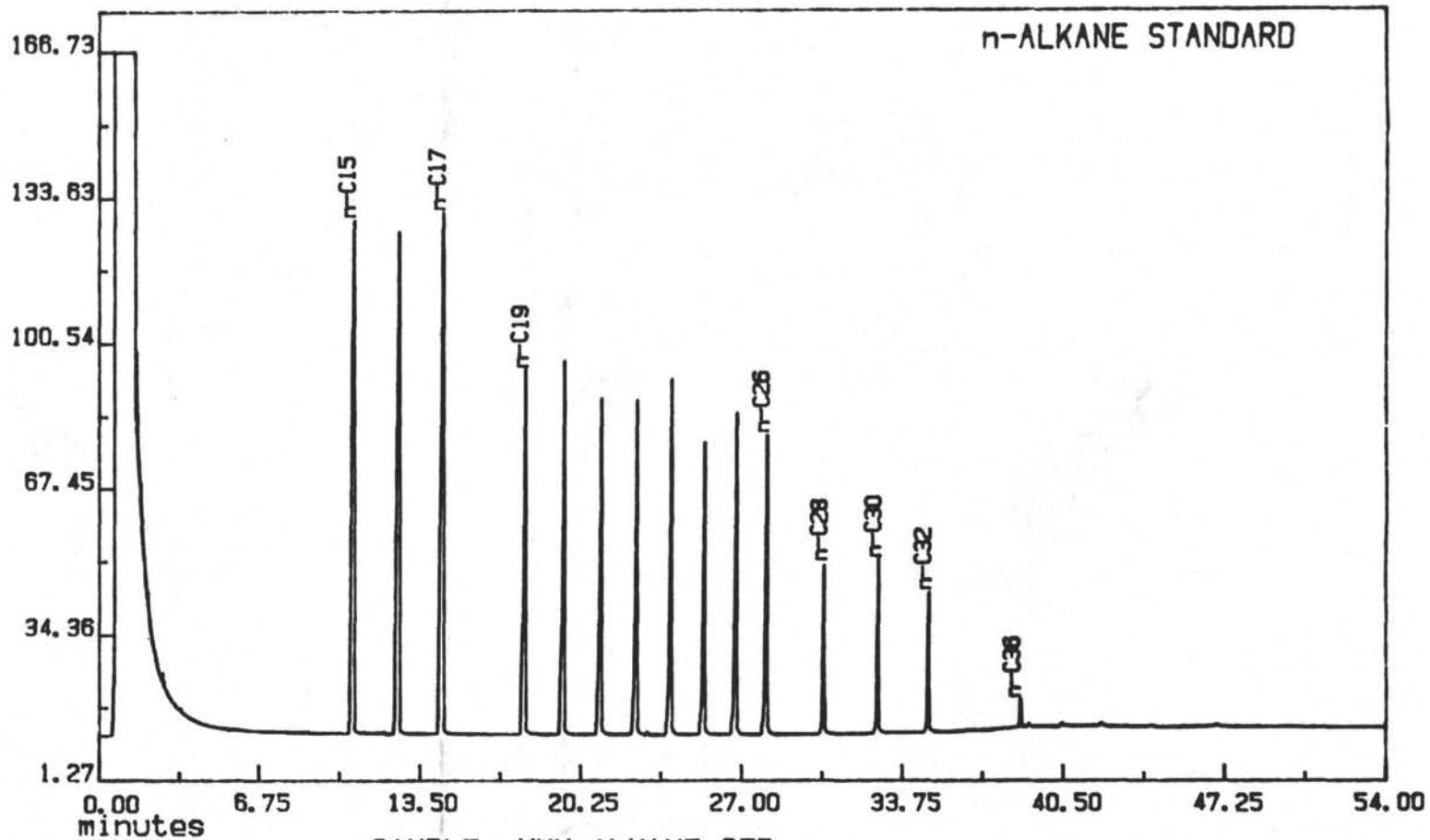
Table A-5. Substances with a very low probability of contaminating cores.

Common/Trade Name	Product Description	Manufacturer	Usage	Wt(mg)
Gear Oil (Fig. A-34)	Lead-free E.P Oil GRXB-220	British Petroleum	For piperacker and other rig equipment	60
Carboline Thinner (Fig. A-35)	Carboline Thinner #10	Carboline St. Louis, Missouri	Paint remover in tool room	70
RTV Silicone Rubber (Fig. A-36)	Adhesive Sealant	General Electric Company Silicone Products Division Waterford, New York	Seal pressure seals or fittings on deck equipment; rarely used down hole.	50
Martin Decker Fluid (Fig. A-37)	Martin Decker Fluid	Martin Decker Dallas, Texas	Weight Indicator sensors, lubricators on rig floor	50

Table A-6. Potential contaminants classified by usage.

DRILLING	CORE EQUIPMENT	LABORATORY
Pipe Dope (Pb)	Parker O-Lube	3-in-One Oil
Pipe Dope (Zn)	Silicone O-ring Grease	WD-40
Line Tar	WD-40	Marking Pencil
Cable Coating	Super Agitene	Jet Lube
GO-JO Hand Cleaner	Multi-grease	Aqua Lube
Multigrease	Lubriplate	All Purpose Lube Oil
Compensator Oil	Never-Seez	GO-JO Hand Cleaner
	E-Z Break	
	7-11 Oil	

AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: HMW ALKANE STD
ANALYZED: Thu Jul 18, 1985 4:34:29 pm
RESULT: /DATA/LOOP/RESULT/ALKANESTD.RES

Figure A-1. Gas chromatogram of a standard n-alkane mixture.

AMPLITUDE/1000 (Enlarged x 3.0)

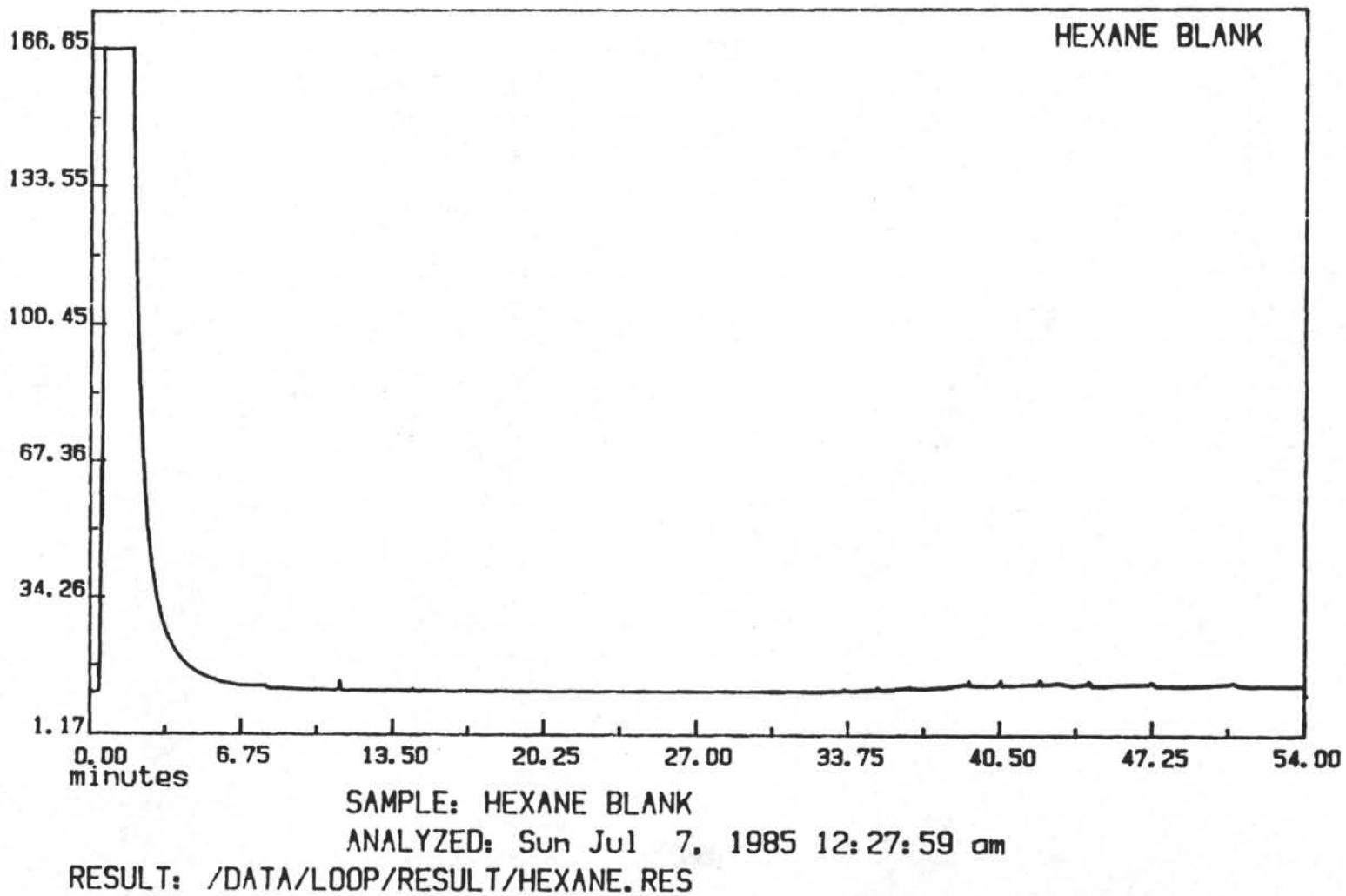
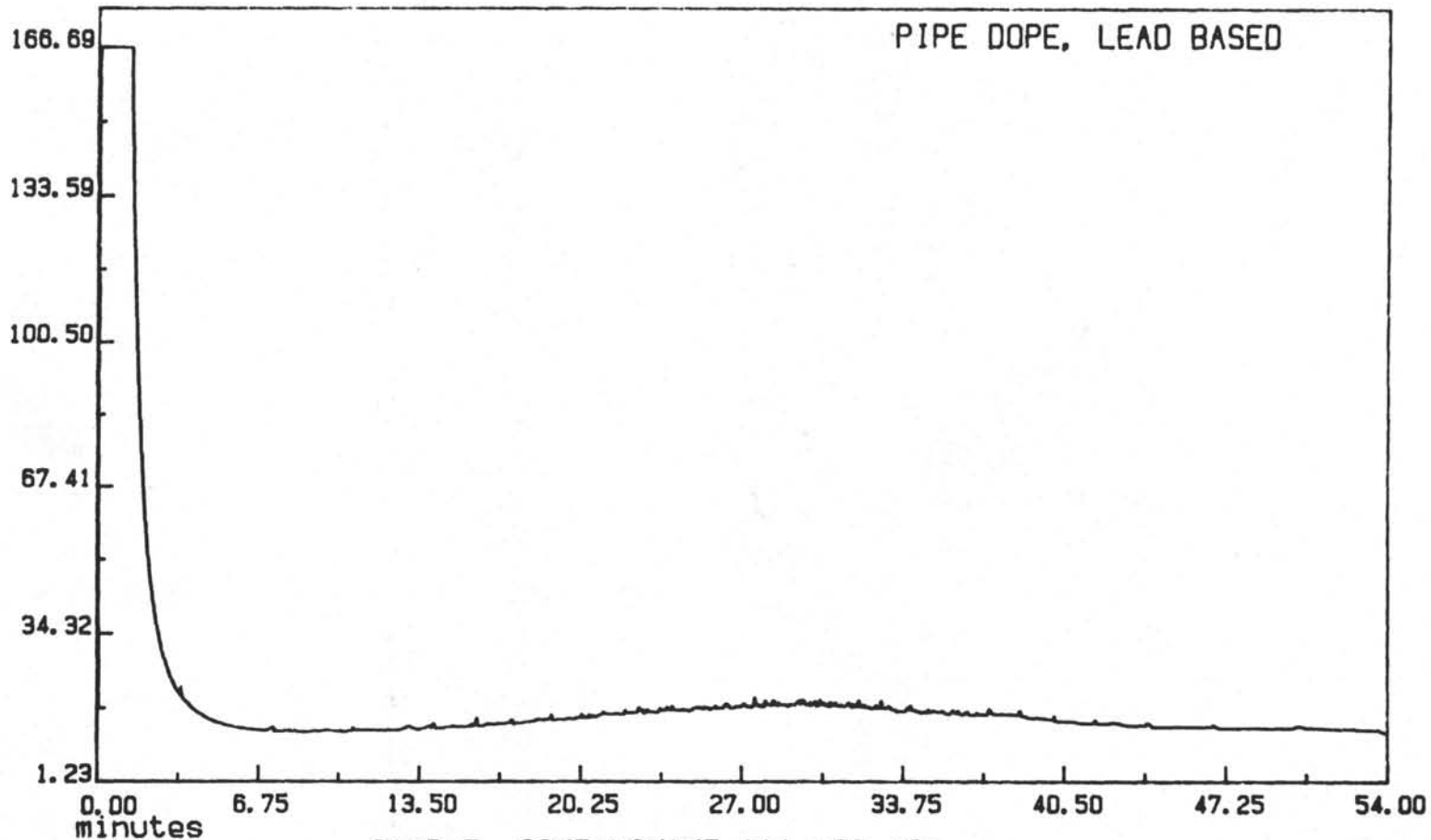


Figure A-2. Gas chromatogram of a hexane blank.

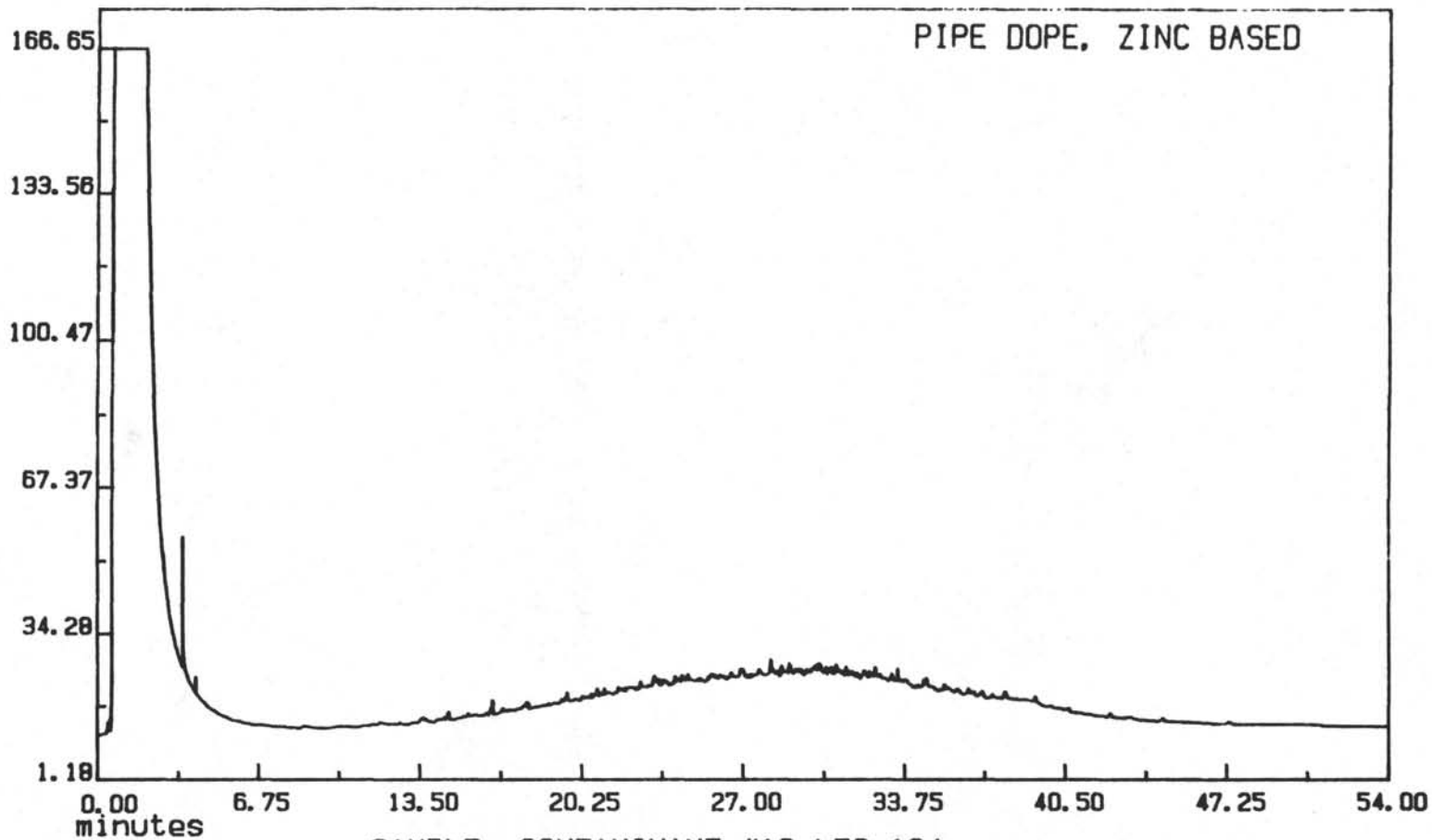
AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: CONTAMINANT #11 LEG 104
ANALYZED: Sun Jul 7, 1985 1:39:44 am
RESULT: /DATA/LOOP/RESULT/CONT11.RES

Figure A-3. Gas chromatogram of Contaminant #11, Leg 104.

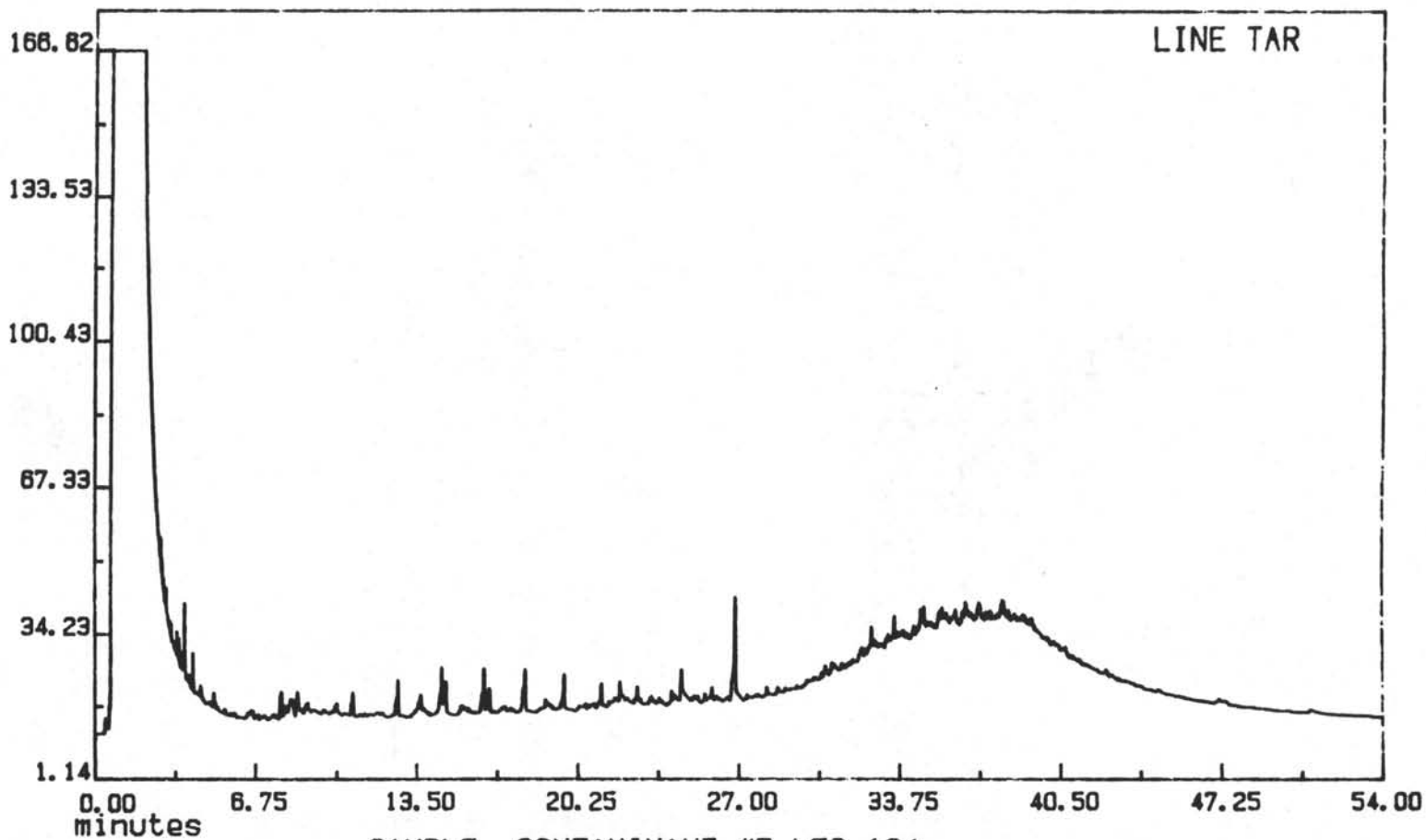
AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: CONTAMINANT #10 LEG 104
ANALYZED: Sat Jul 6, 1985 11:04:19 am
RESULT: /DATA/LOOP/RESULT/CONT10.RES

Figure A-4. Gas chromatogram of Contaminant #10, Leg 104.

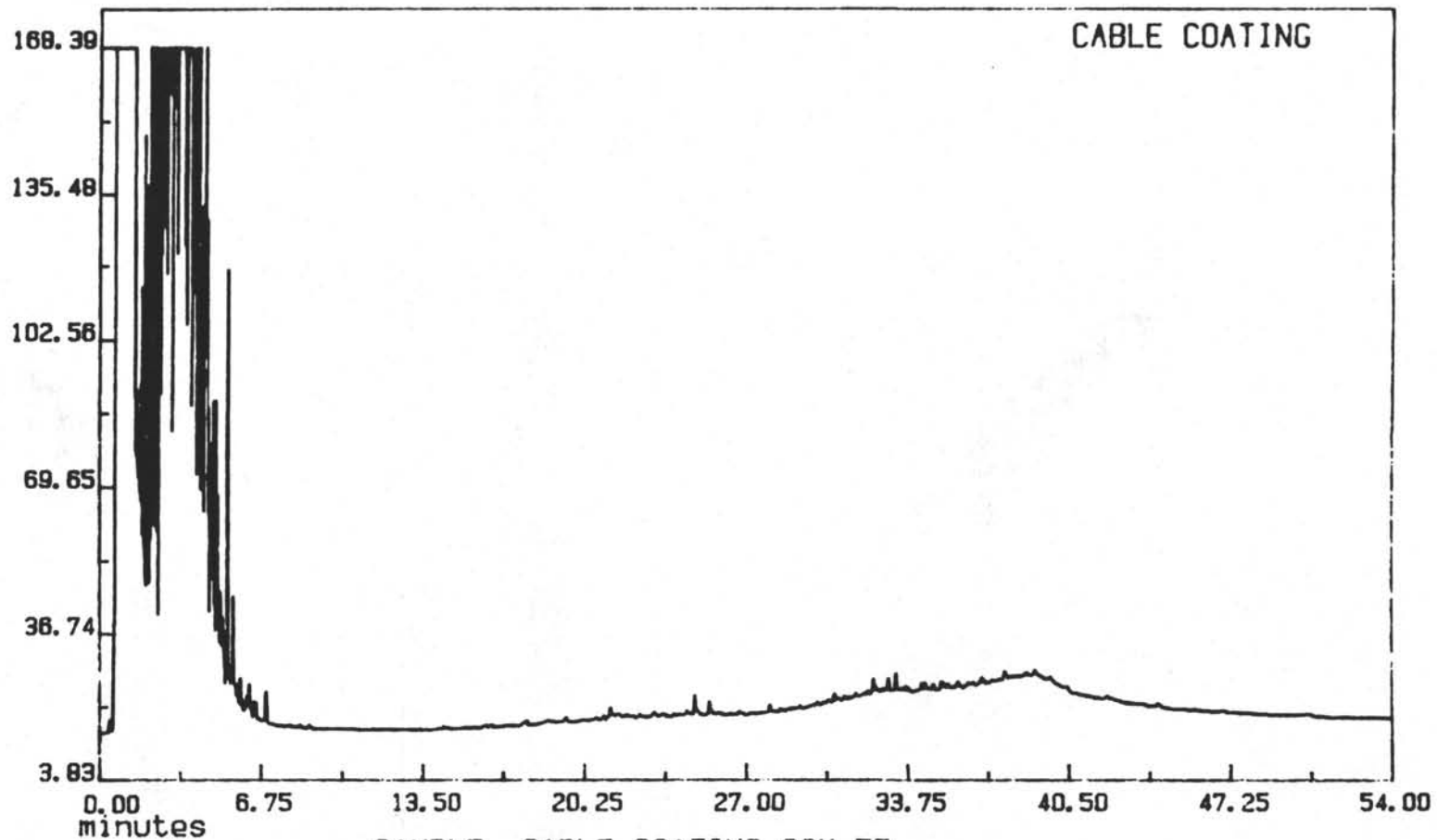
AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: CONTAMINANT #7 LEG 104
ANALYZED: Sat Jul 6, 1985 7:09:30 pm
RESULT: /DATA/LOOP/RESULT/CONT7.RES

Figure A-5. Gas chromatogram of Contaminant #7, Leg 104.

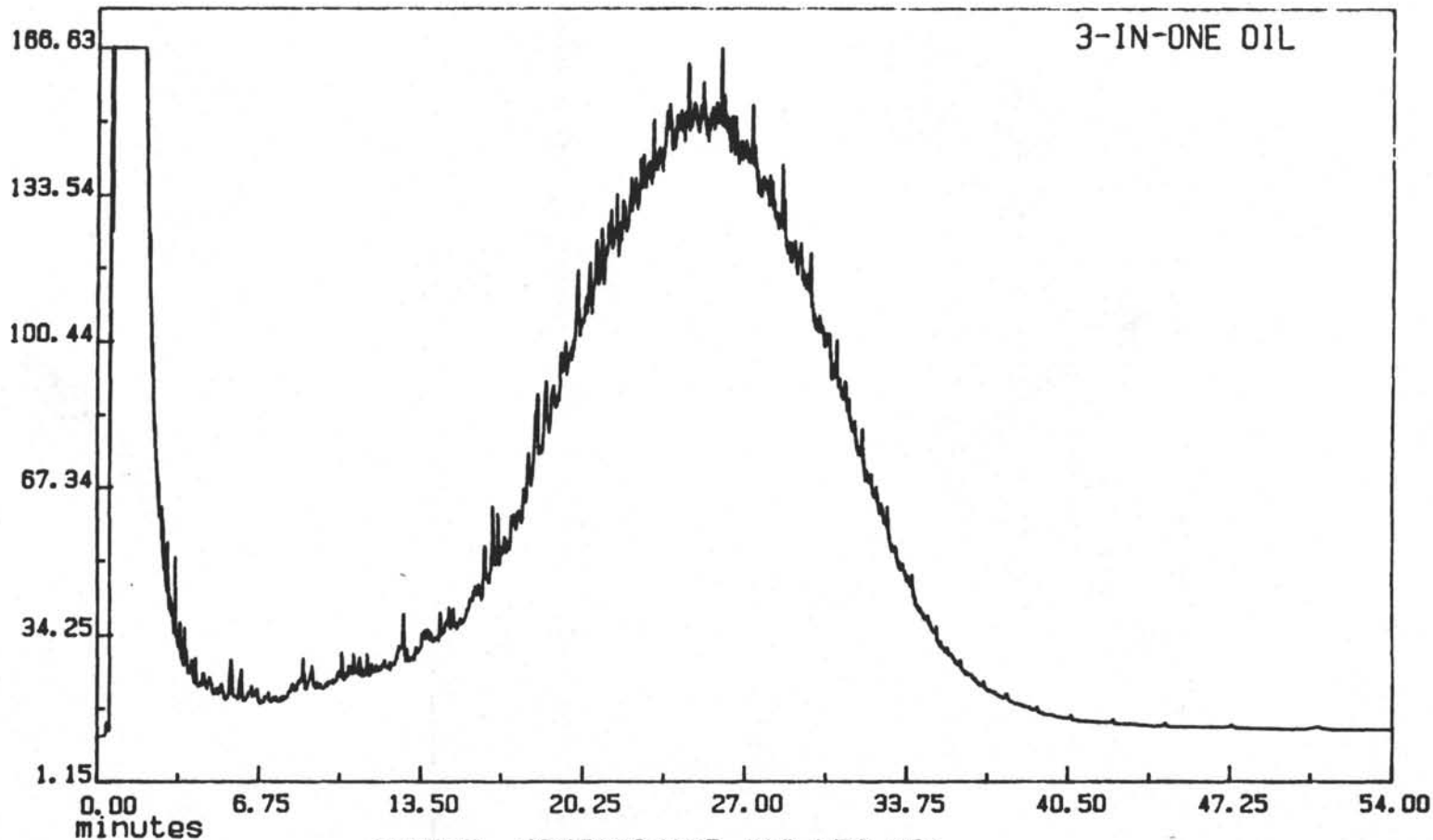
AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: CABLE COATING CCX-77
ANALYZED: Sat Jul 20, 1985 1:11:15 am
RESULT: /DATA/LOOP/RESULT/CONT39.RES

Figure A-6. Gas chromatogram of Cable Coating CCX-77.

AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: CONTAMINANT #13 LEG 104
ANALYZED: Sat Jul 6, 1985 3:03:40 pm
RESULT: /DATA/LOOP/RESULT/CONT13.RES

Figure A-7. Gas chromatogram of Contaminant #13, Leg 104.

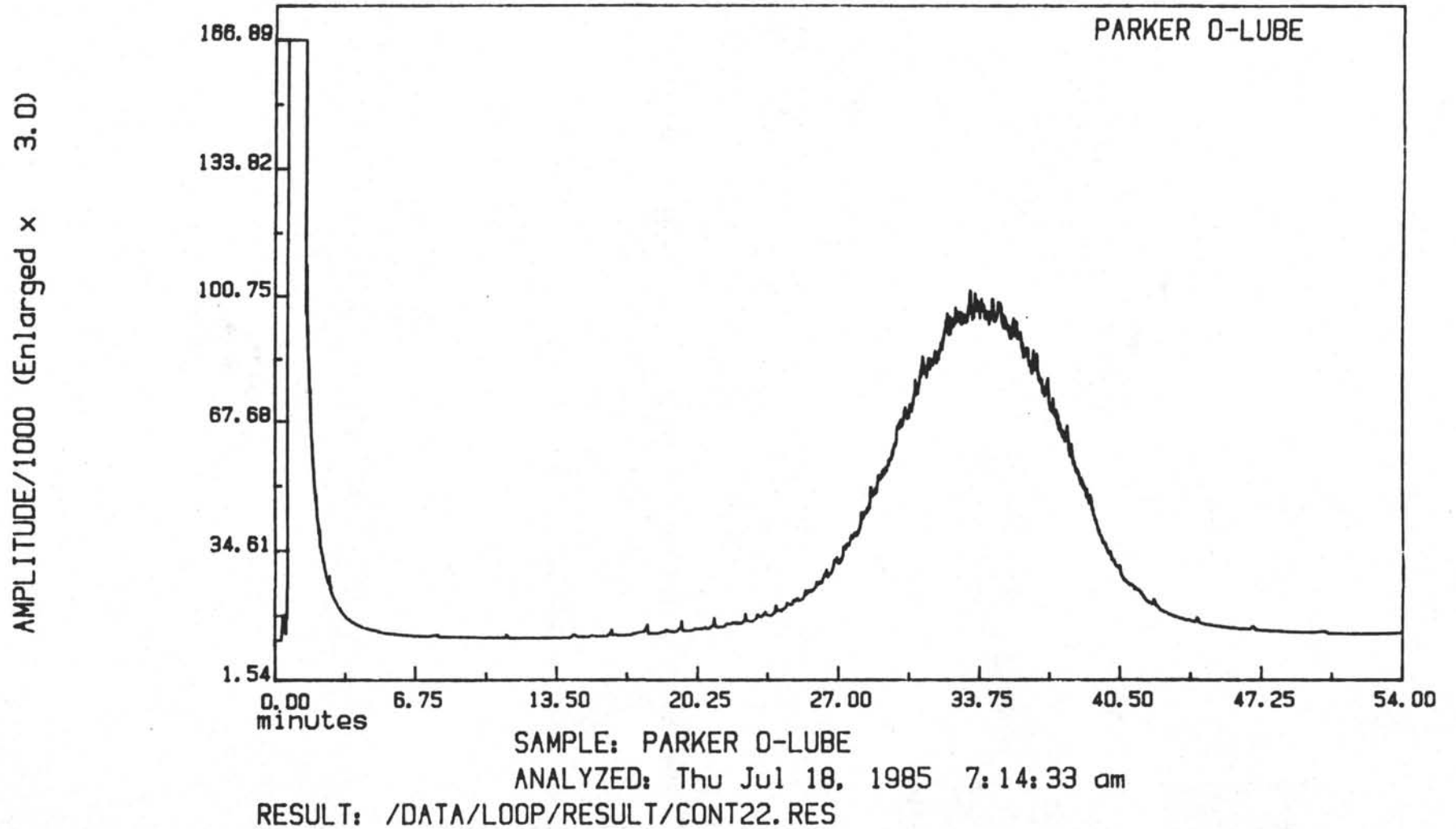
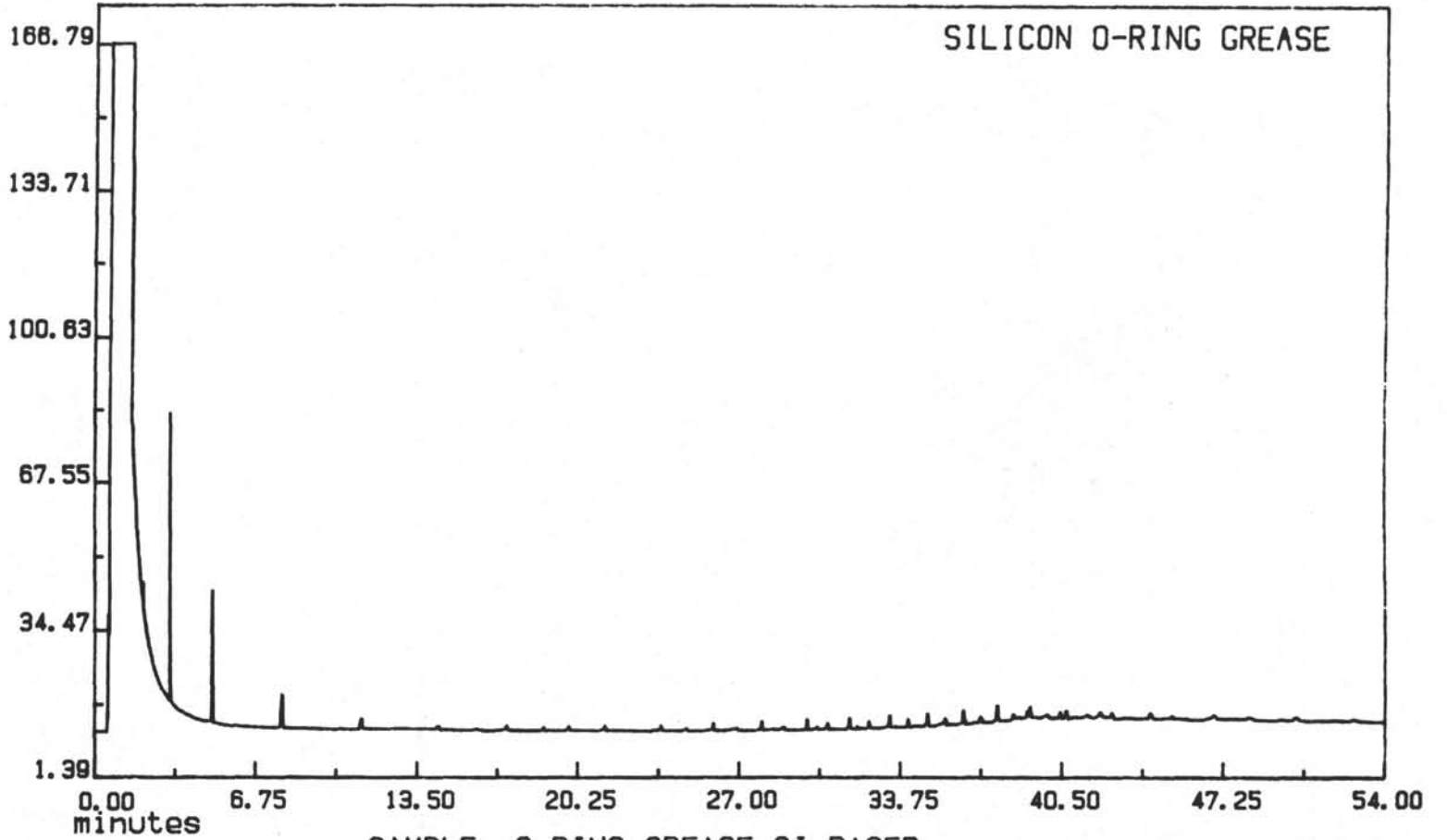


Figure A-8. Gas chromatogram of Parker O-Lube.

AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: O-RING GREASE SI BASED
ANALYZED: Thu Jul 18, 1985 2:20:24 pm
RESULT: /DATA/LOOP/RESULT/CONT17.RES

Figure A-9. Gas chromatogram of O-Ring Grease, SI Based.

AMPLITUDE/1000 (Enlarged x 3.0)

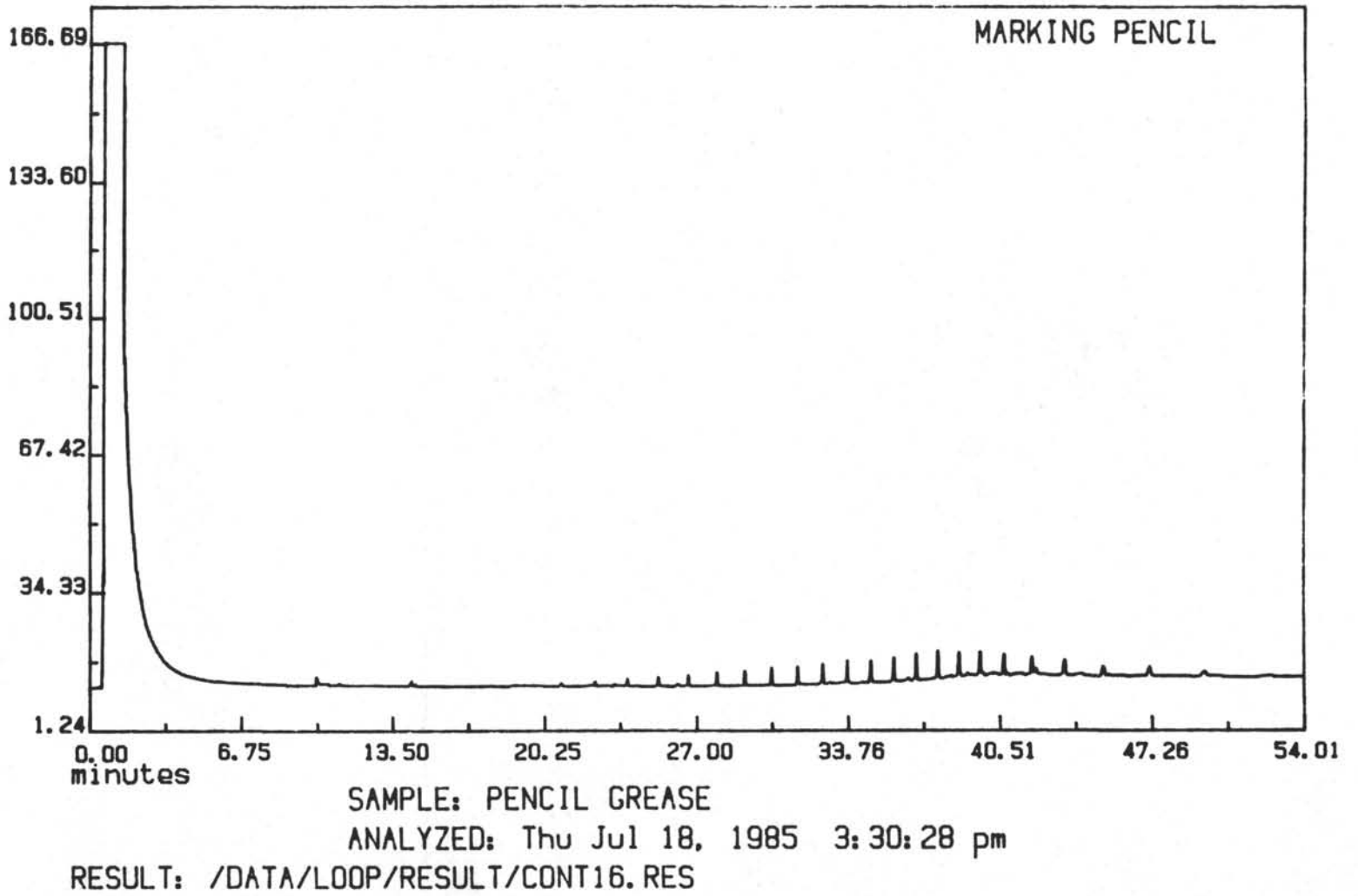


Figure A-10. Gas chromatogram of Pencil Grease.

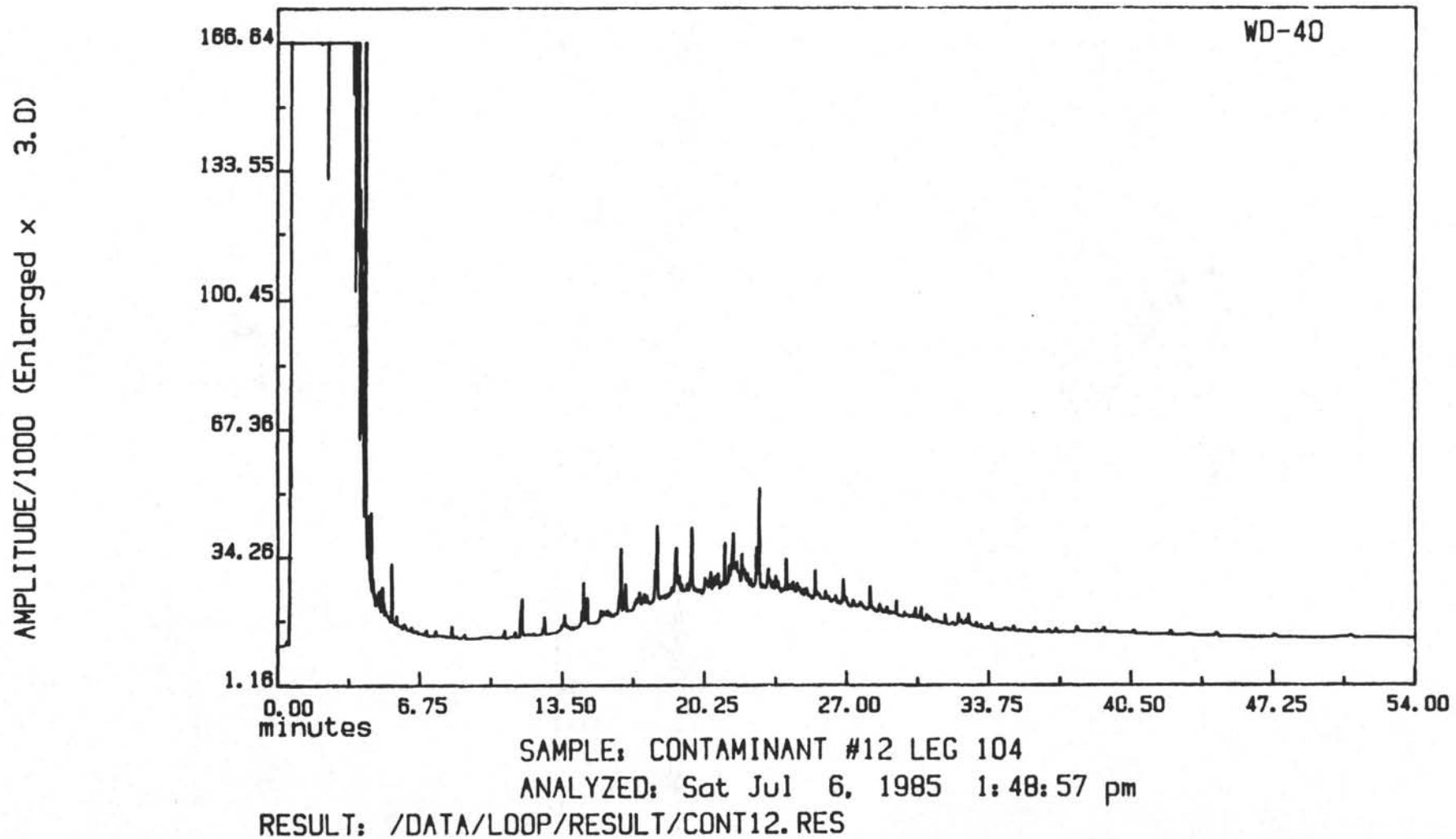
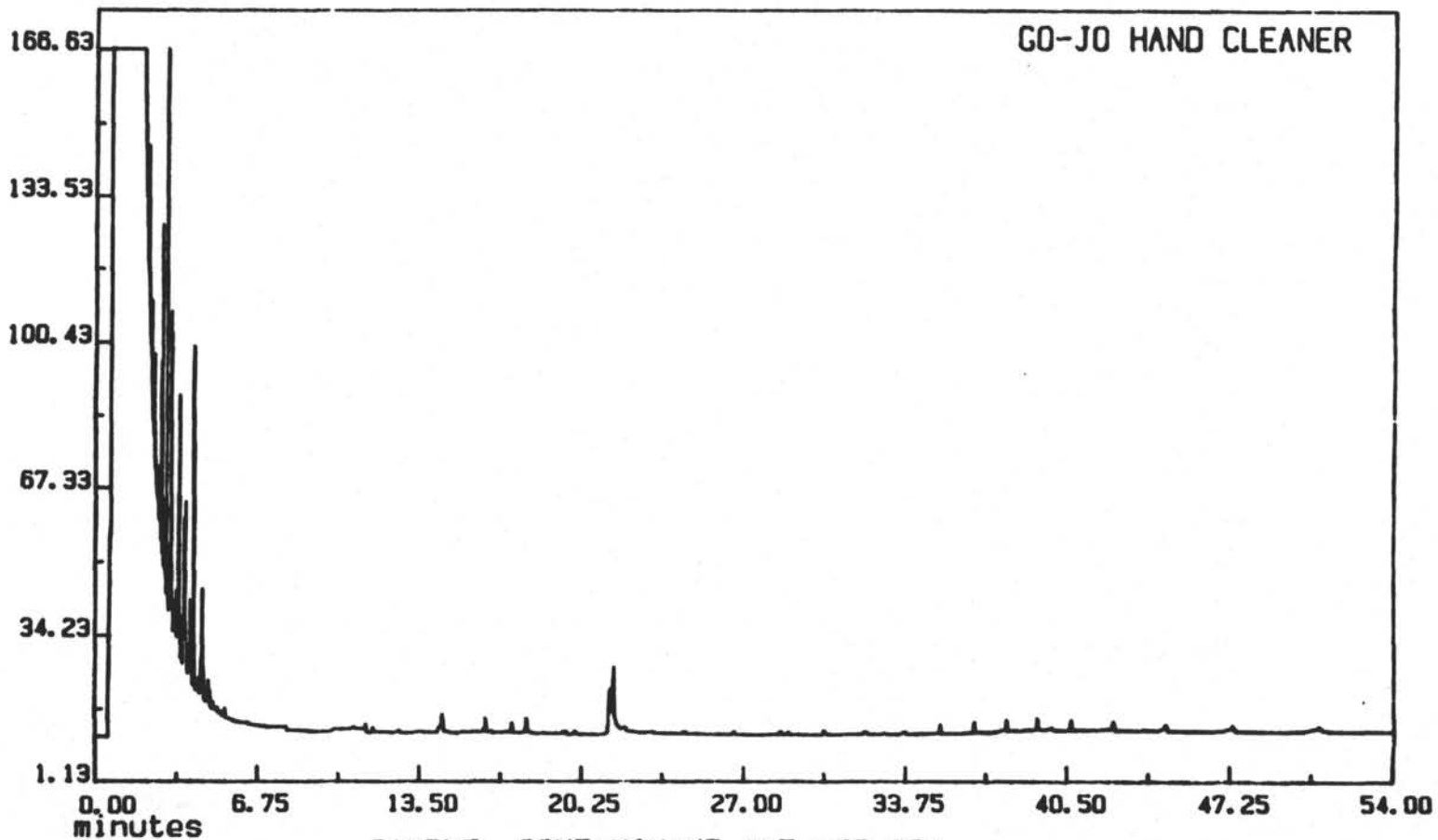


Figure A-11. Gas chromatogram of Contaminant #12, Leg 104.

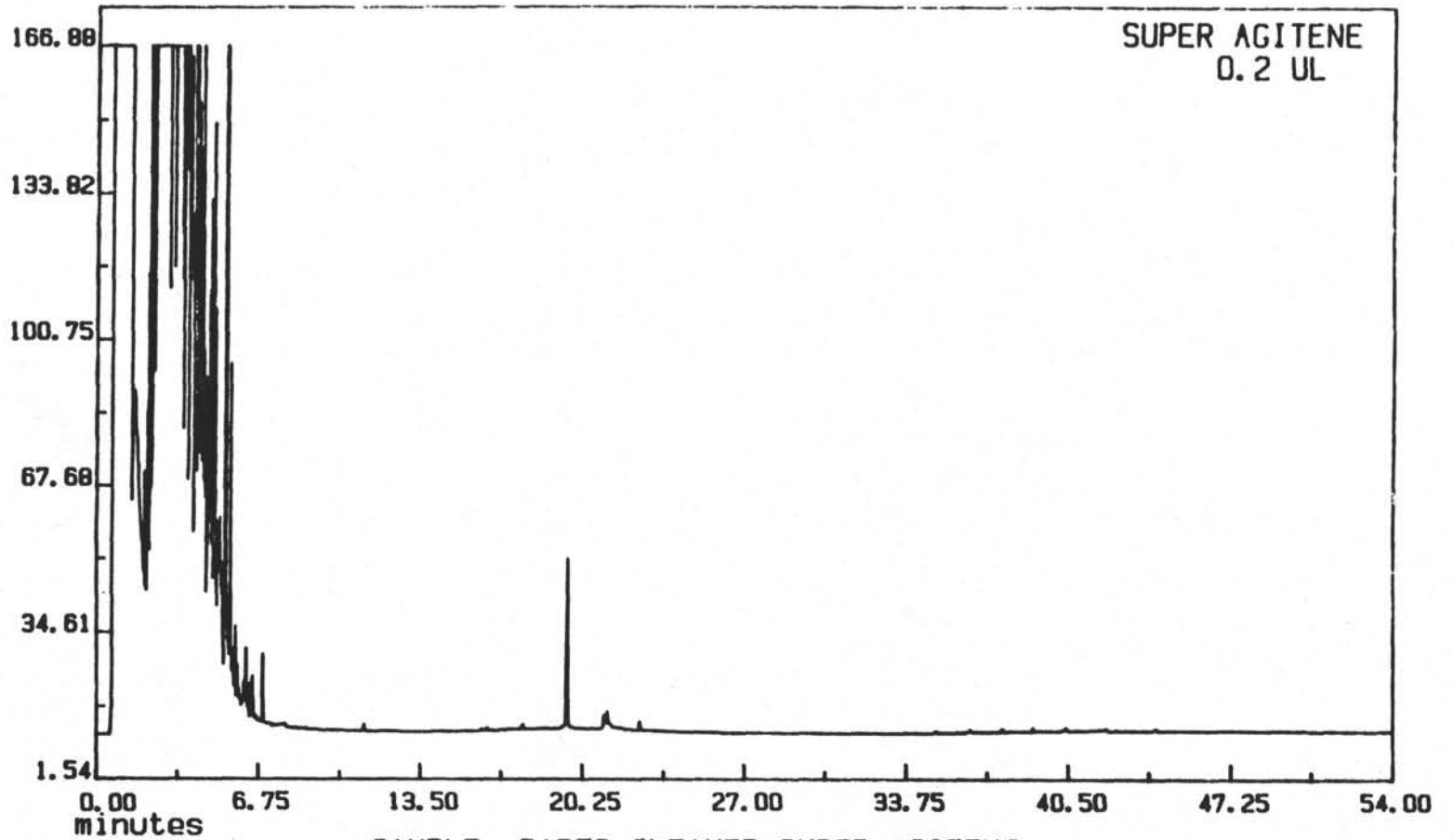
AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: CONTAMINANT #15 LEG 104
ANALYZED: Sun Jul 7, 1985 9:05:35 am
RESULT: /DATA/LOOP/RESULT/CONT15.RES

Figure A-12. Gas chromatogram of Contaminant #15, Leg 104.

AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: PARTS CLEANER SUPER AGITENE
ANALYZED: Thu Jul 18, 1985 10:54:16 am
RESULT: /DATA/LOOP/RESULT/CONT20.RES

Figure A-13. Gas chromatogram of Parts Cleaner Super Agitene.

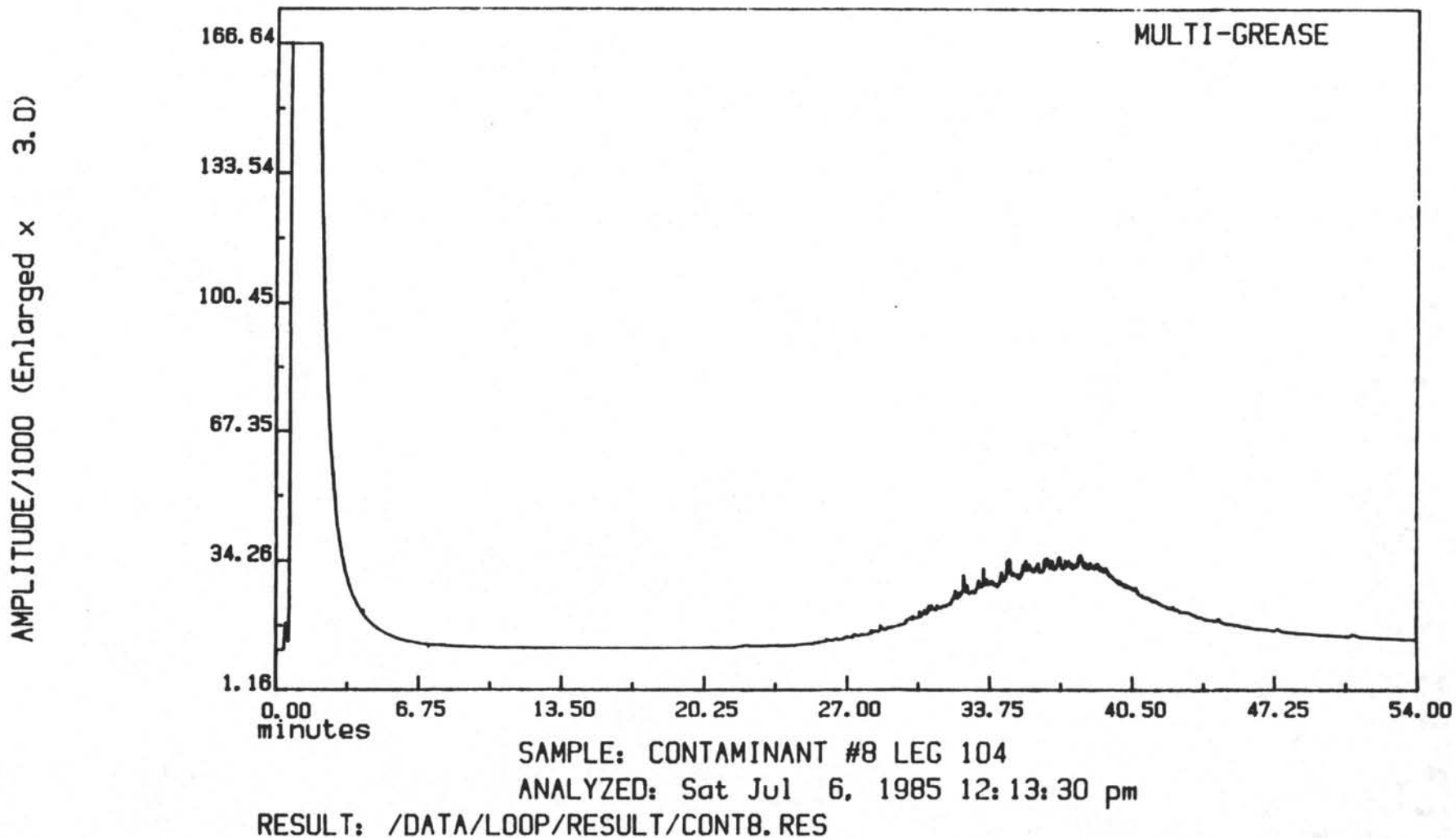


Figure A-14. Gas chromatogram of Contaminant #8, Leg 104.

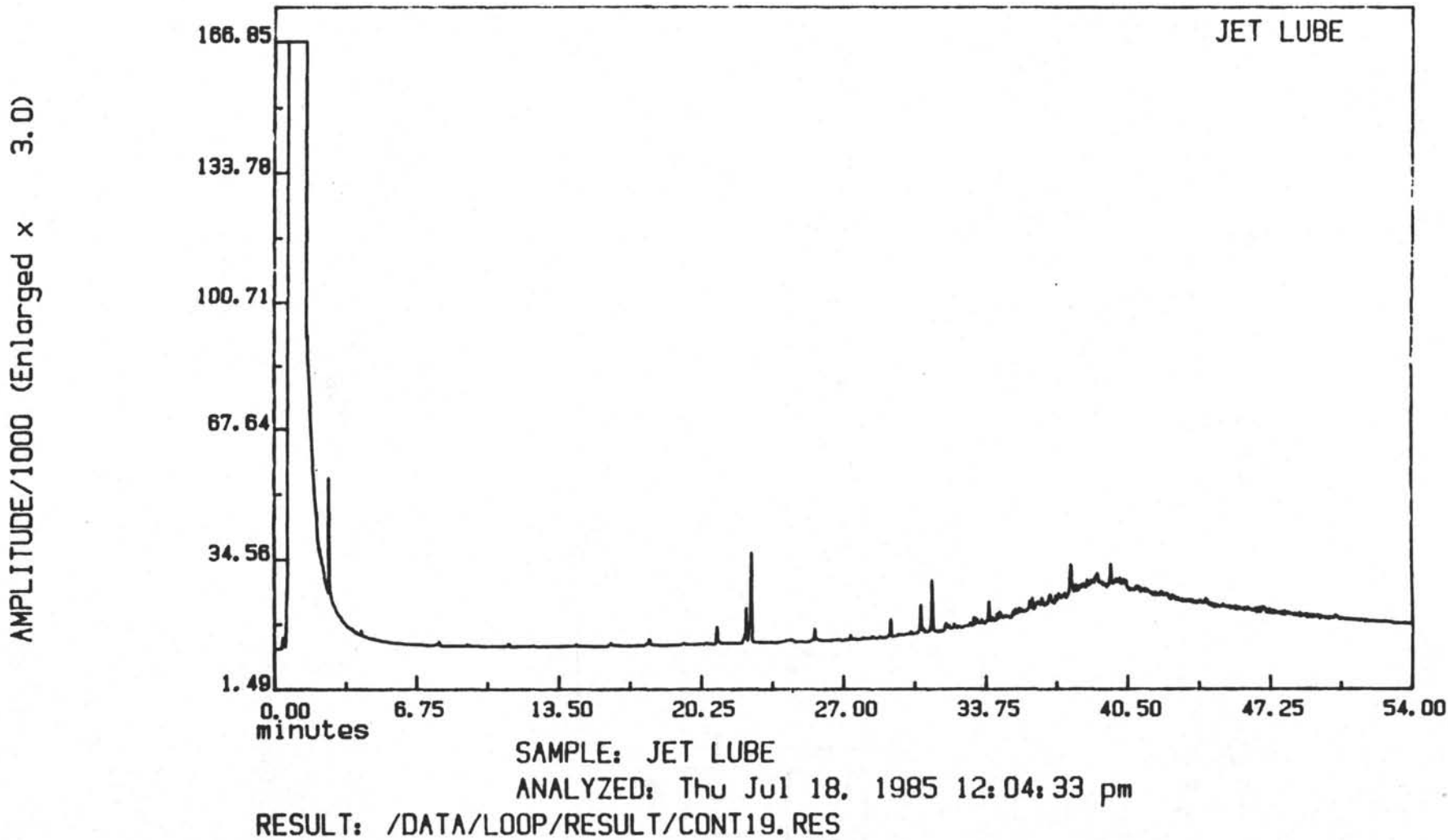
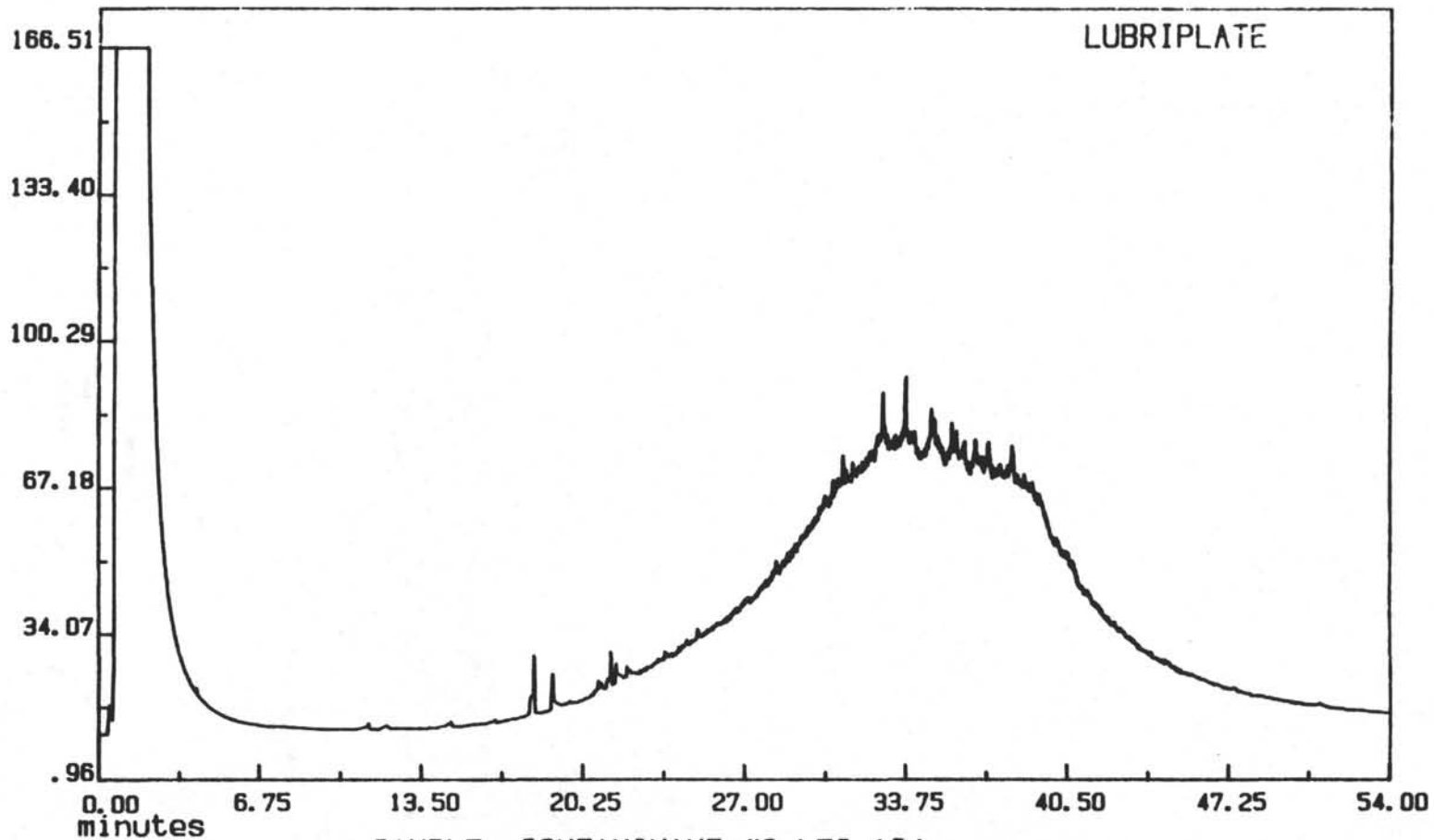


Figure A-15. Gas chromatogram of Jet Lube.

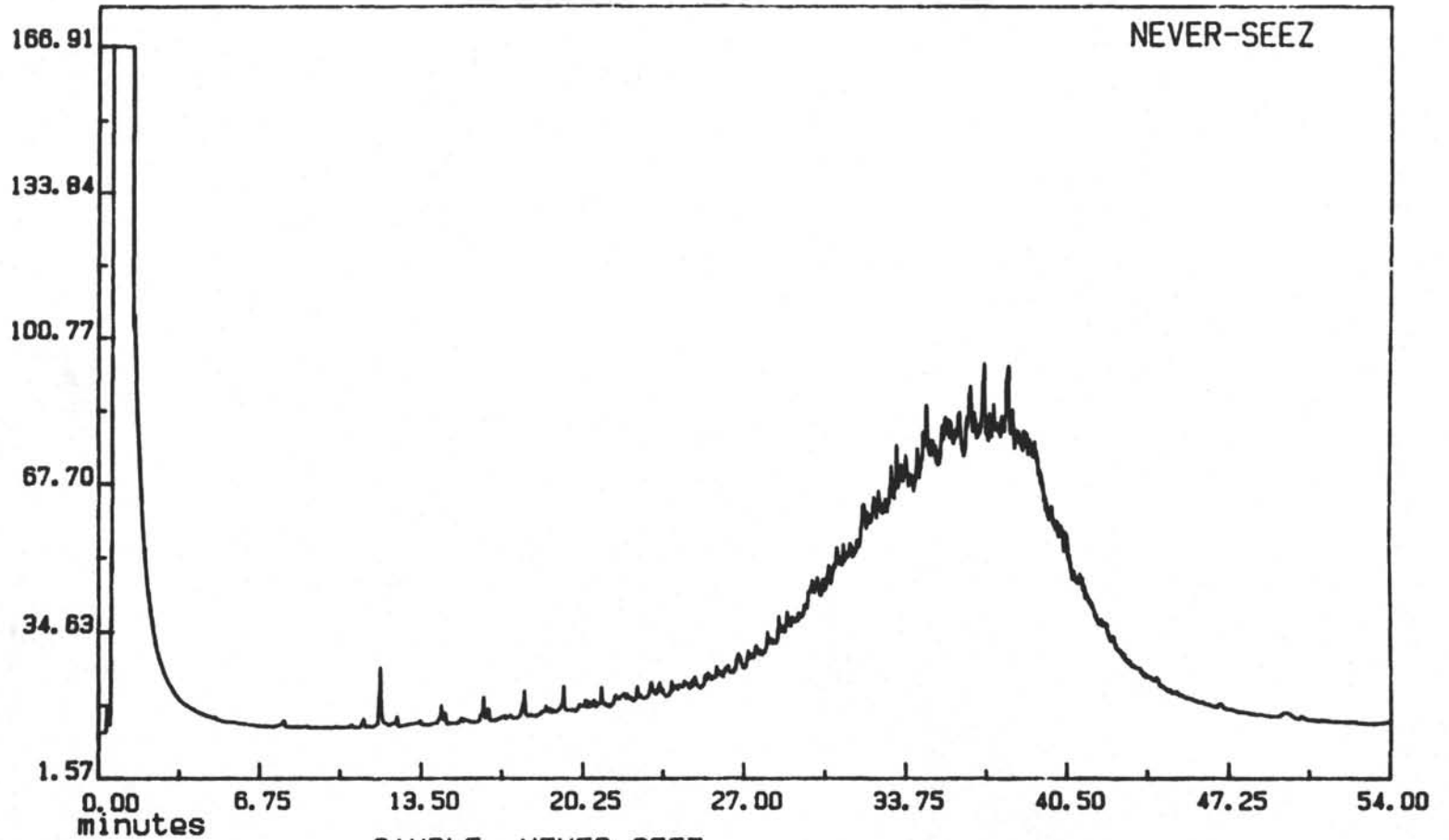
AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: CONTAMINANT #9 LEG 104
ANALYZED: Sat Jul 6, 1985 5:54:02 pm
RESULT: /DATA/LOOP/RESULT/CONT9.RES

Figure A-16. Gas chromatogram of Contaminant #9, Leg 104.

AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: NEVER SEEZ
ANALYZED: Thu Jul 18, 1985 6:01:11 am
RESULT: /DATA/LOOP/RESULT/CONT23.RES

Figure A-17. Gas chromatogram of Never Seez.

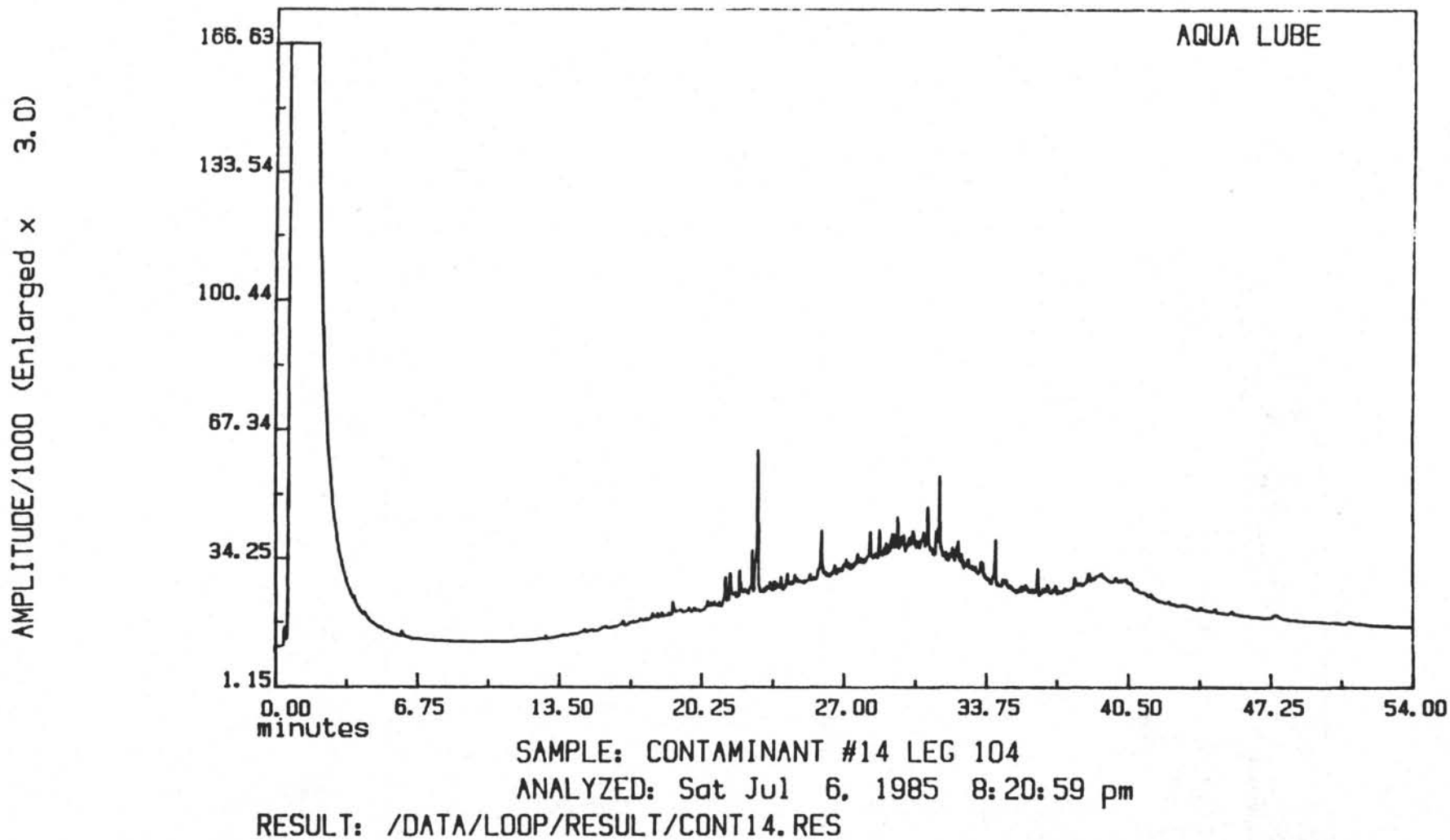


Figure A-18. Gas chromatogram of Contaminant #14, Leg 104.

AMPLITUDE/1000 (Enlarged x 3.0)

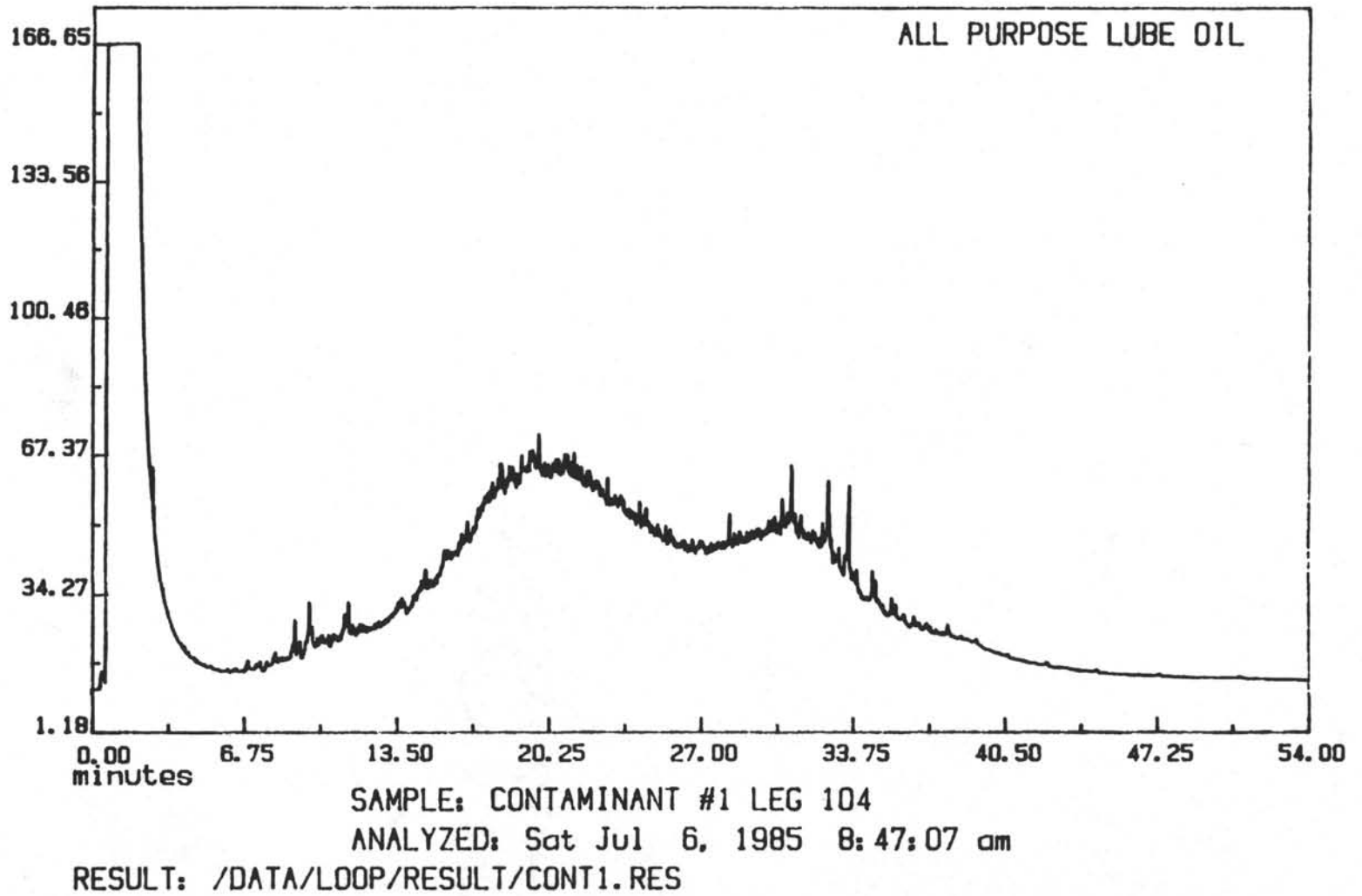
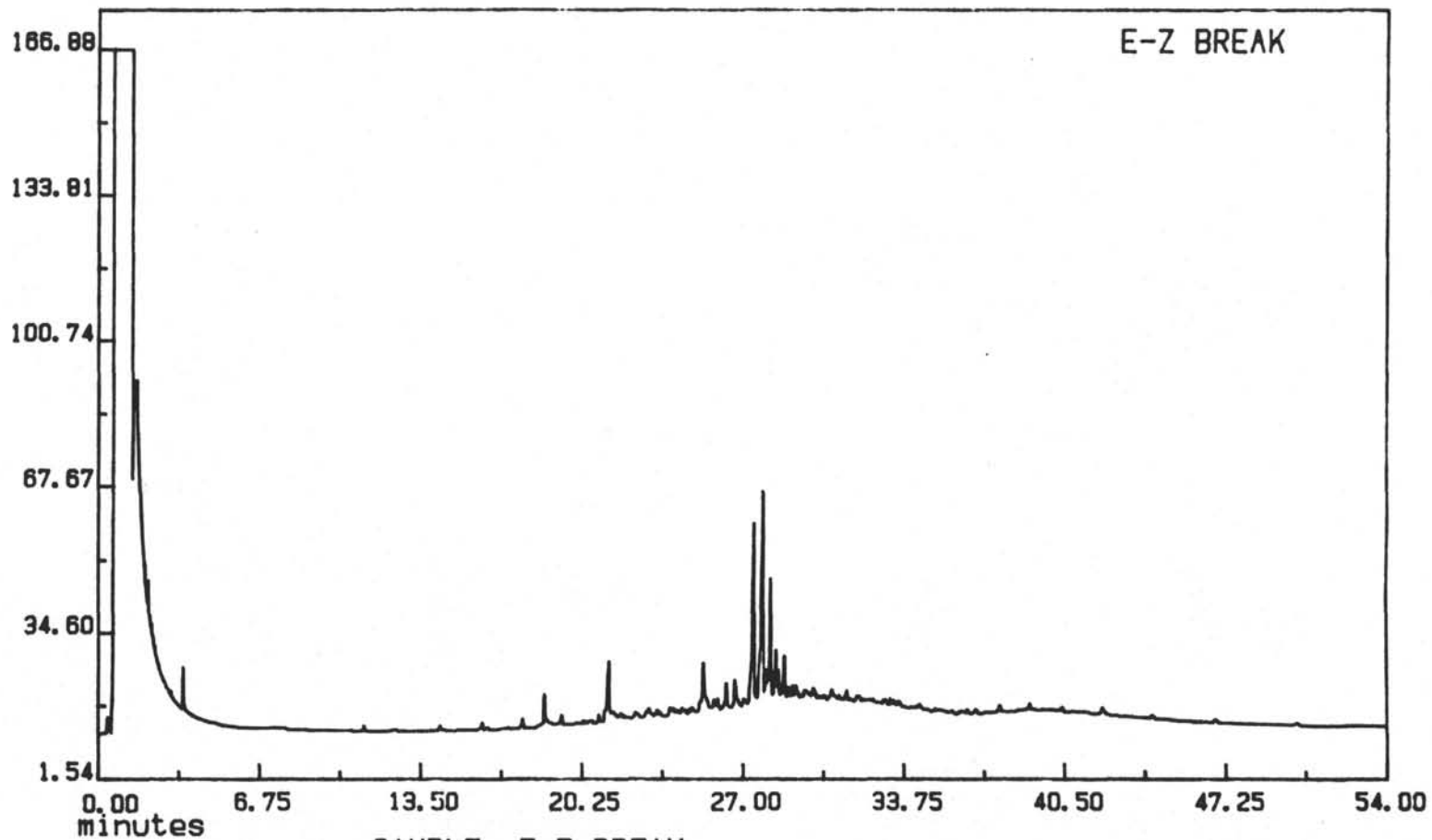


Figure A-19. Gas chromatogram of Contaminant #1, Leg 104.

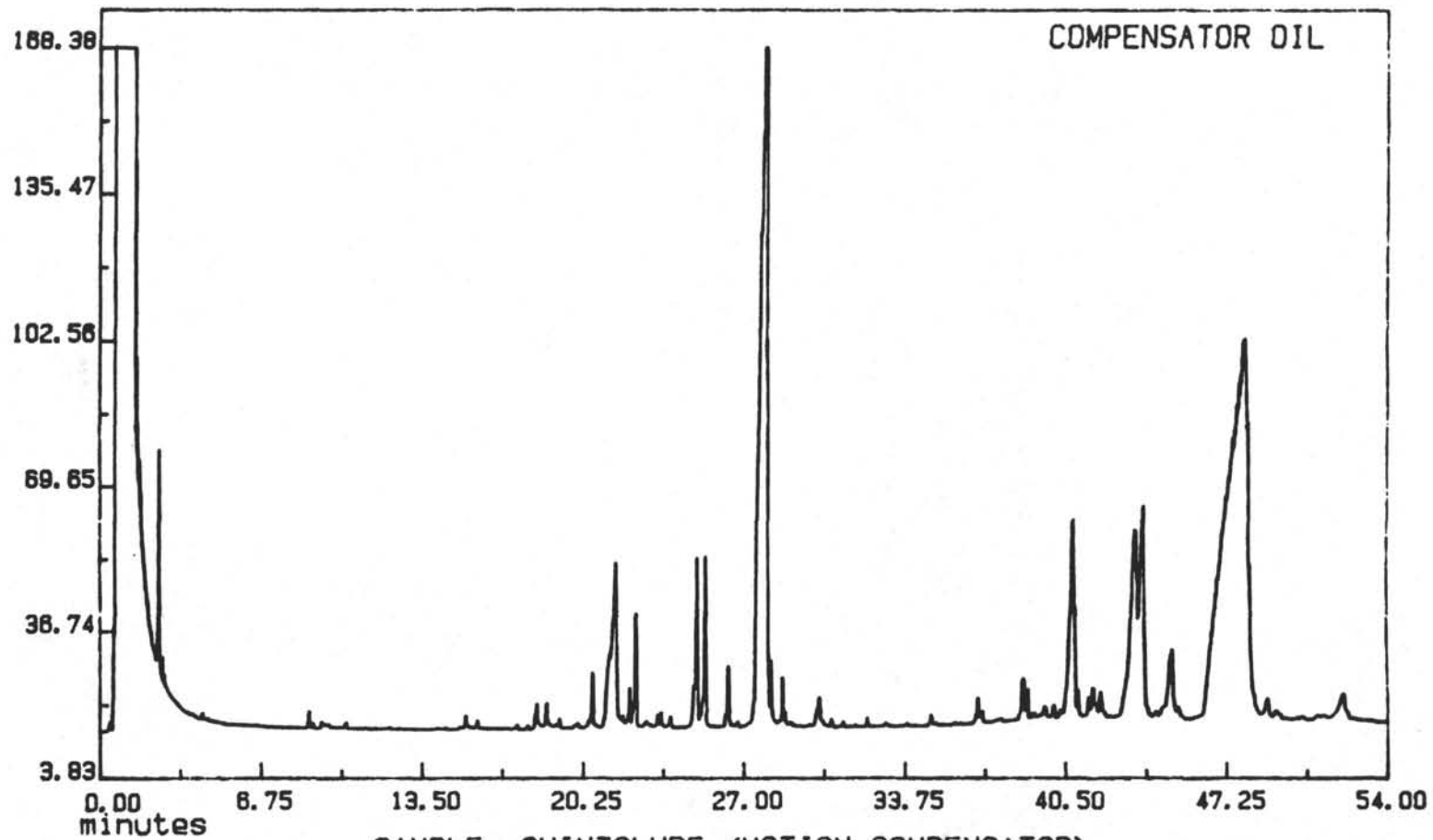
AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: E-Z BREAK
ANALYZED: Thu Jul 18, 1985 8:27:58 am
RESULT: /DATA/LOOP/RESULT/CONT21.RES

Figure A-20. Gas chromatogram of E-Z Break.

AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: QUINTOLUBE (MOTION COMPENSATOR)
ANALYZED: Fri Jul 19, 1985 10:41:38 pm
RESULT: /DATA/LOOP/RESULT/CONT38.RES

Figure A-21. Gas chromatogram of Quintolube (Motion Compensator).

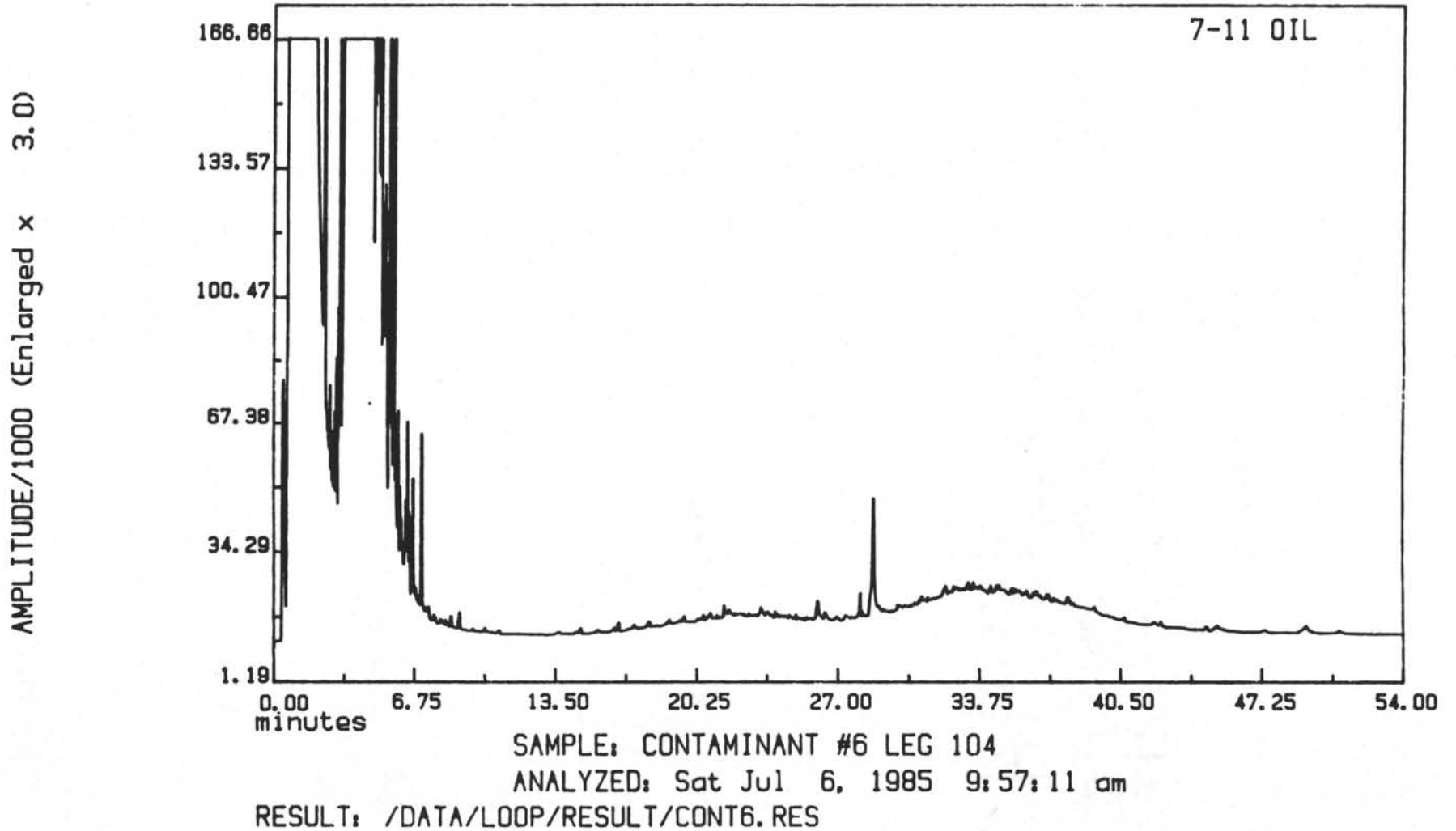
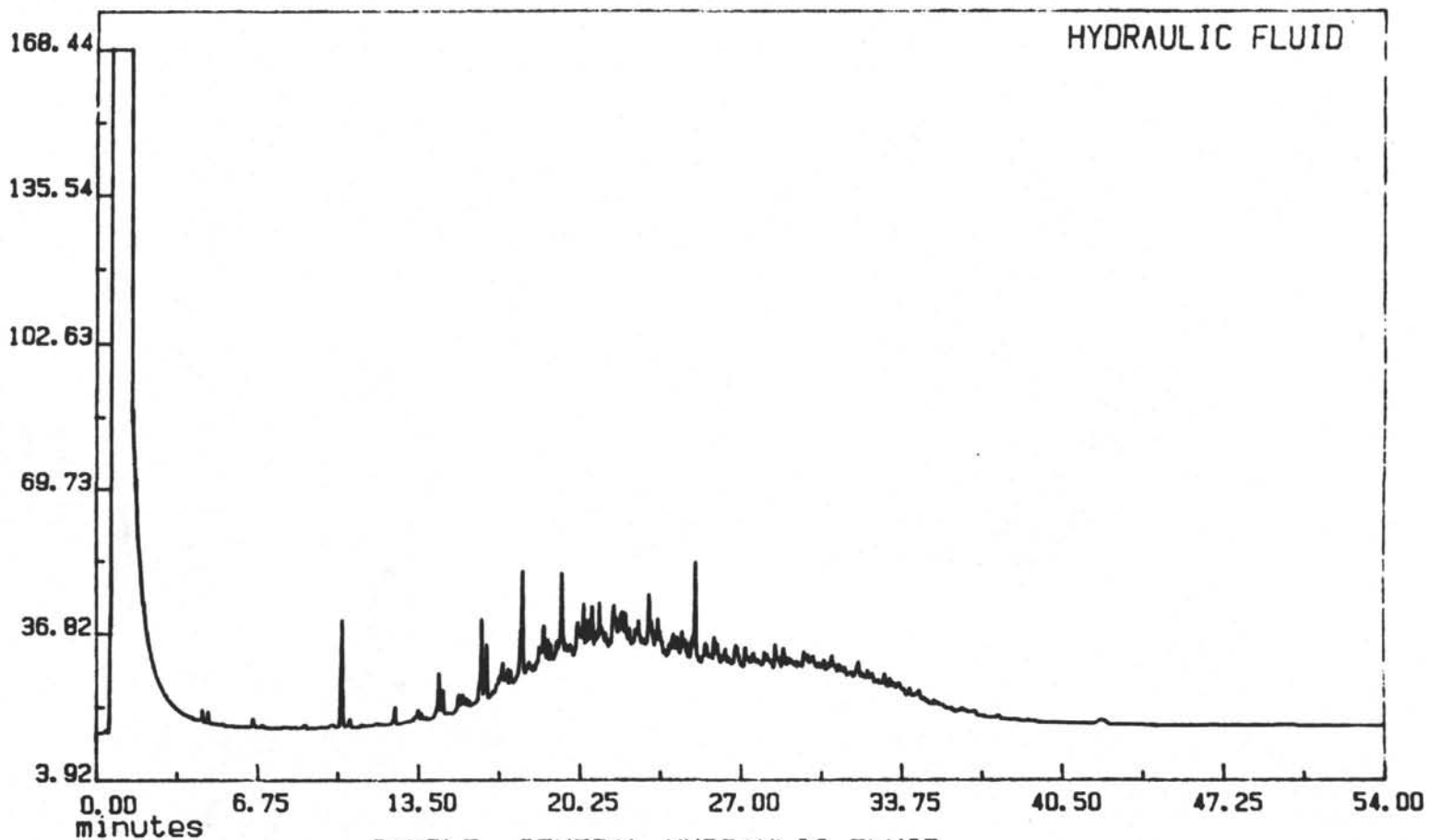


Figure A-22. Gas chromatogram of Contaminant #6, Leg 104.

AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: GENERAL HYDRAULIC FLUID
ANALYZED: Fri Jul 19, 1985 8:06:50 pm
RESULT: /DATA/LOOP/RESULT/CONT36.RES

Figure A-23. Gas chromatogram of General Hydraulic Fluid.

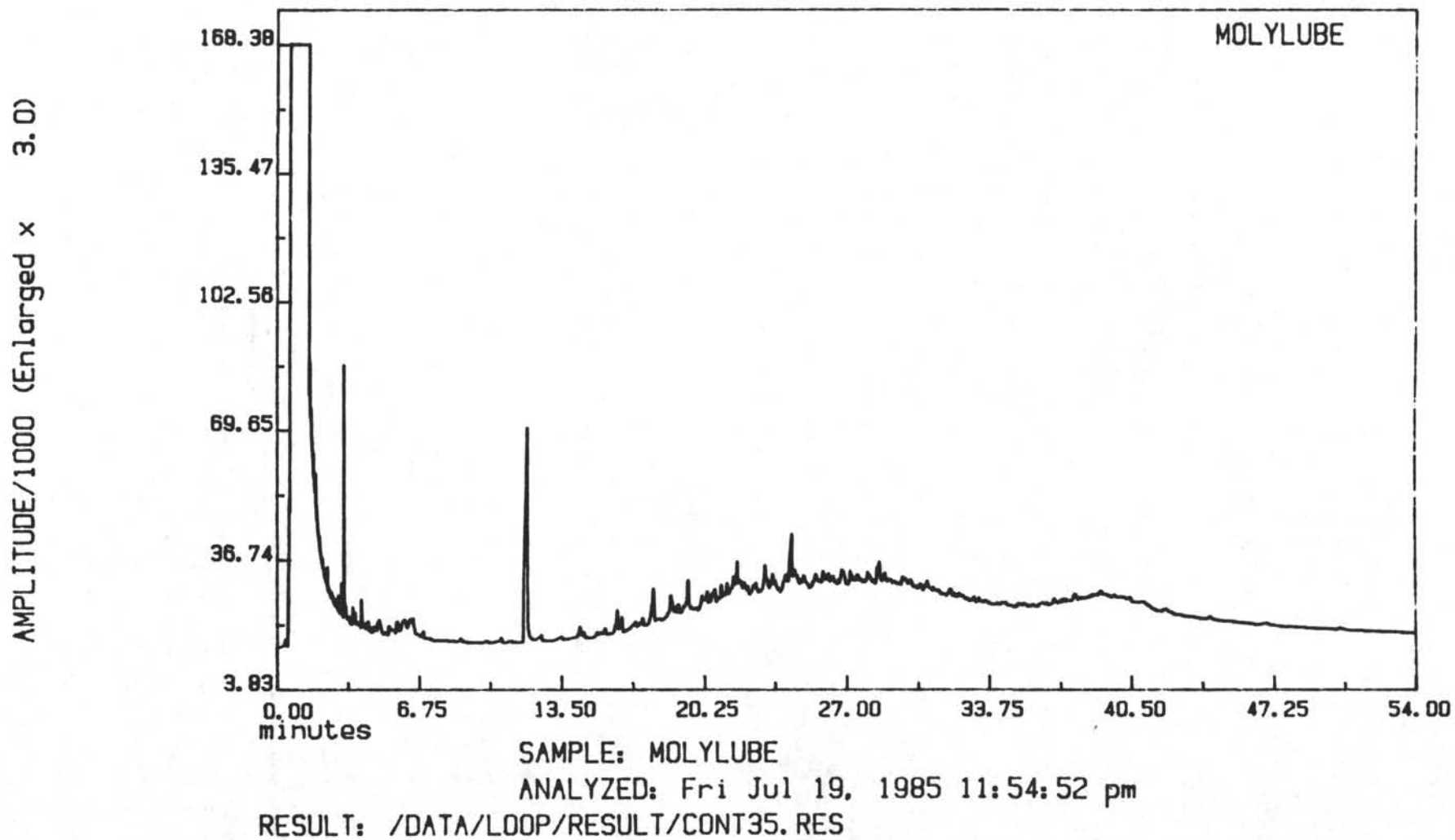
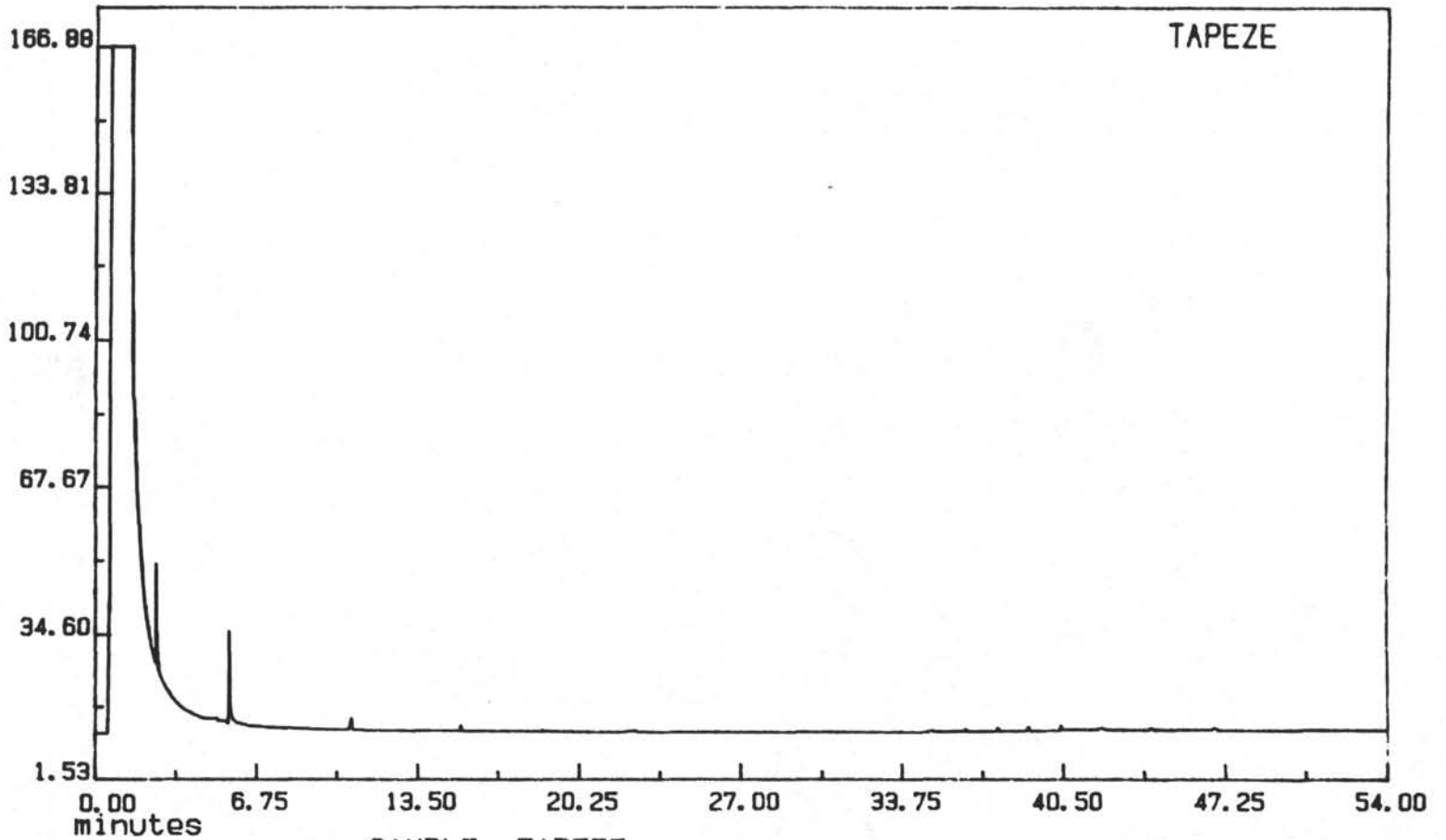


Figure A-24. Gas chromatogram of Molylube.

AMPLITUDE/1000 (Enlarged x 3.0)



TAPEZE

SAMPLE: TAPEZE

ANALYZED: Thu Jul 18, 1985 12:28:58 am

RESULT: /DATA/LOOP/RESULT/CONT25.RES

Figure A-25. Gas chromatogram of Tapeze.

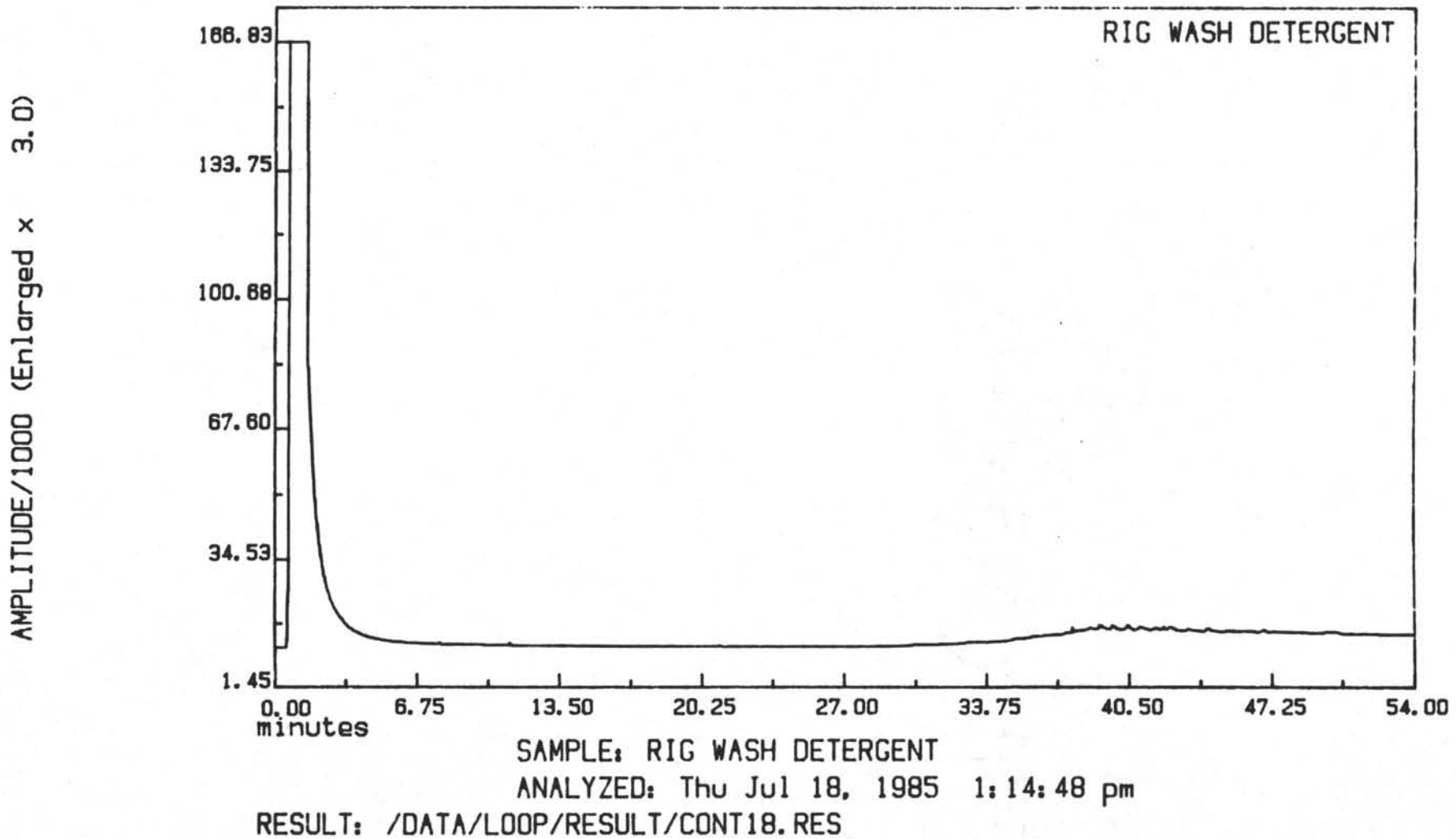
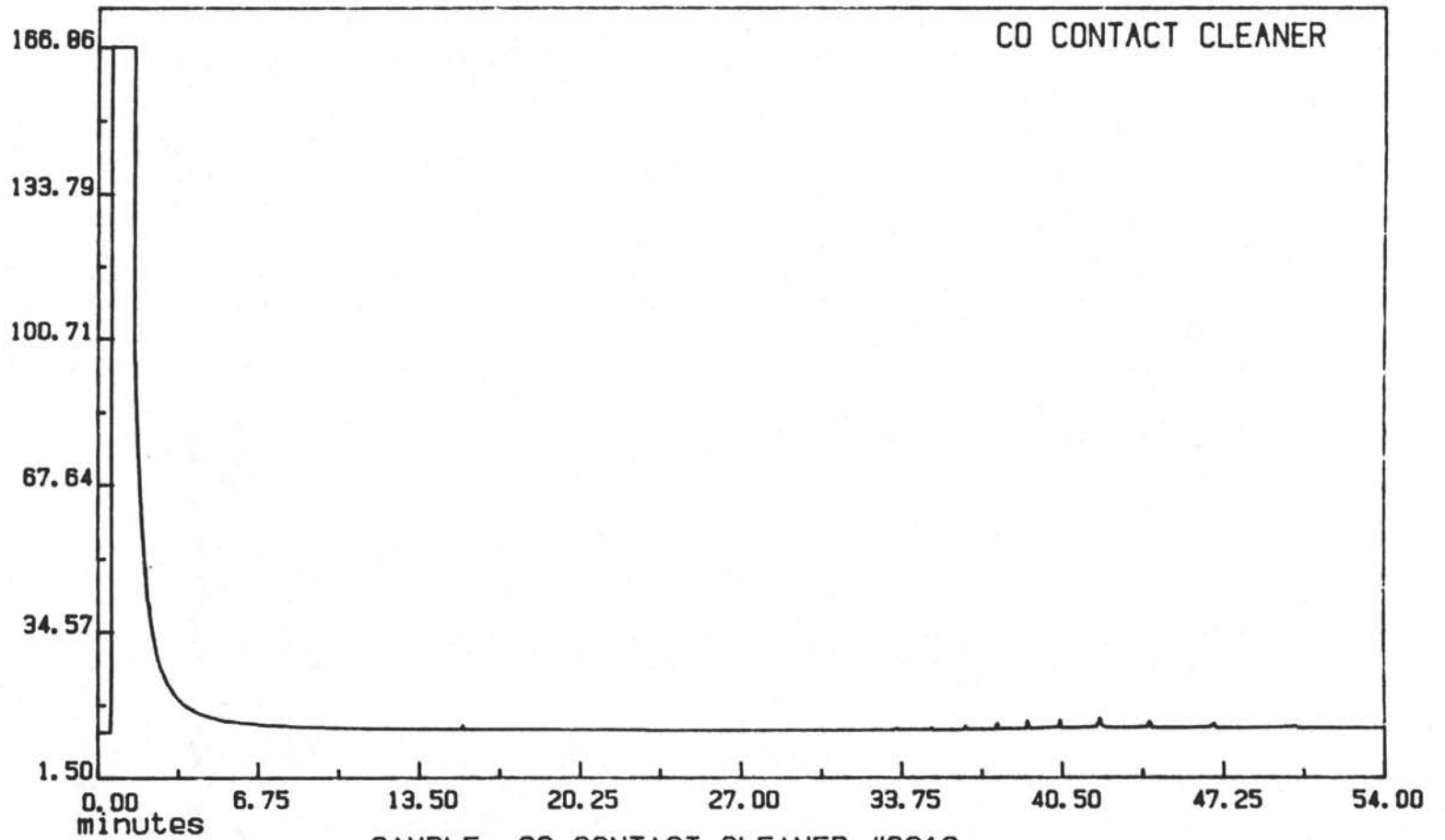


Figure A-26. Gas chromatogram of Rig Wash Detergent.

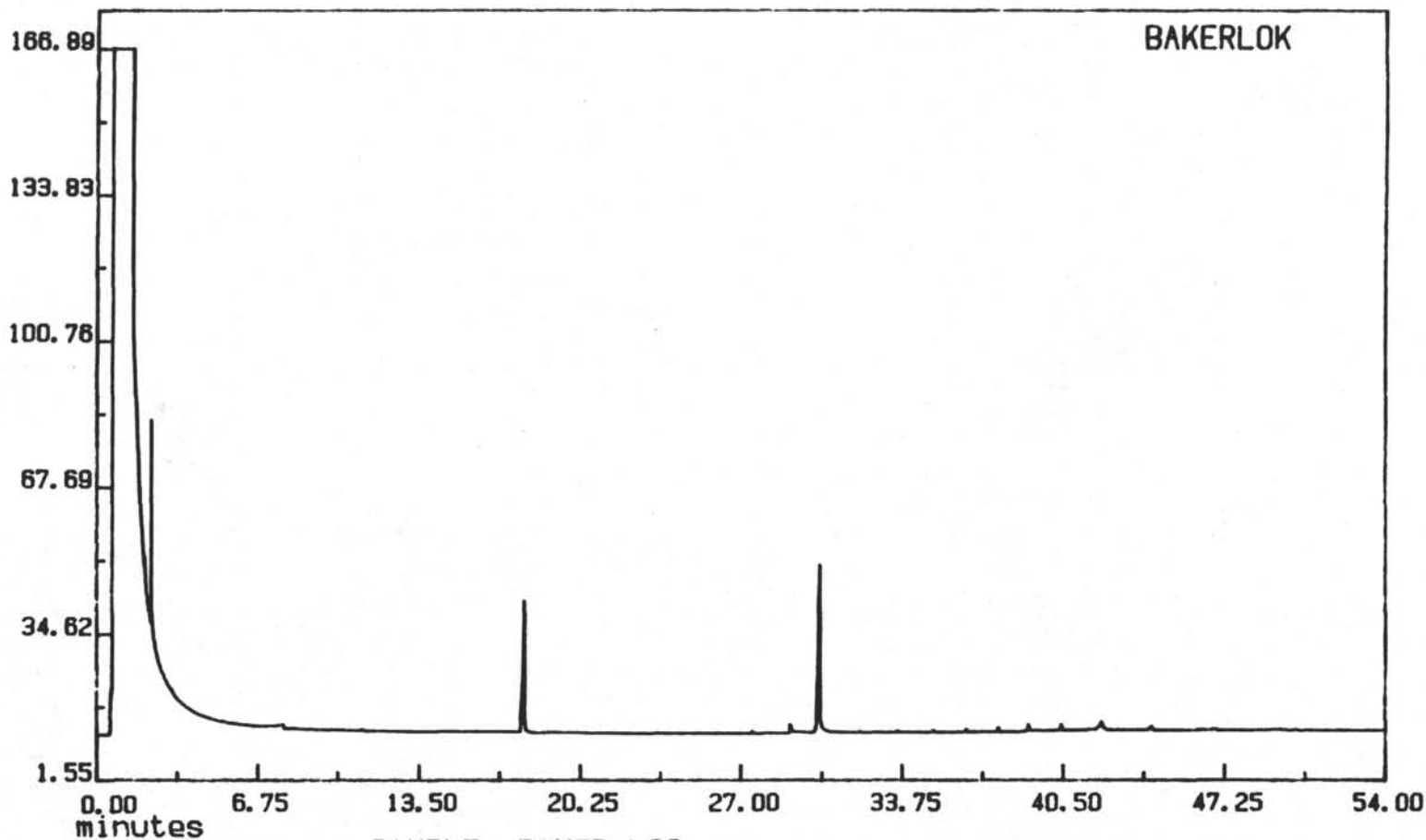
AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: CO CONTACT CLEANER #2016
ANALYZED: Wed Jul 17, 1985 11:21:48 pm
RESULT: /DATA/LOOP/RESULT/CONT26.RES

Figure A-27. Gas chromatogram of CO Contact Cleaner #2016.

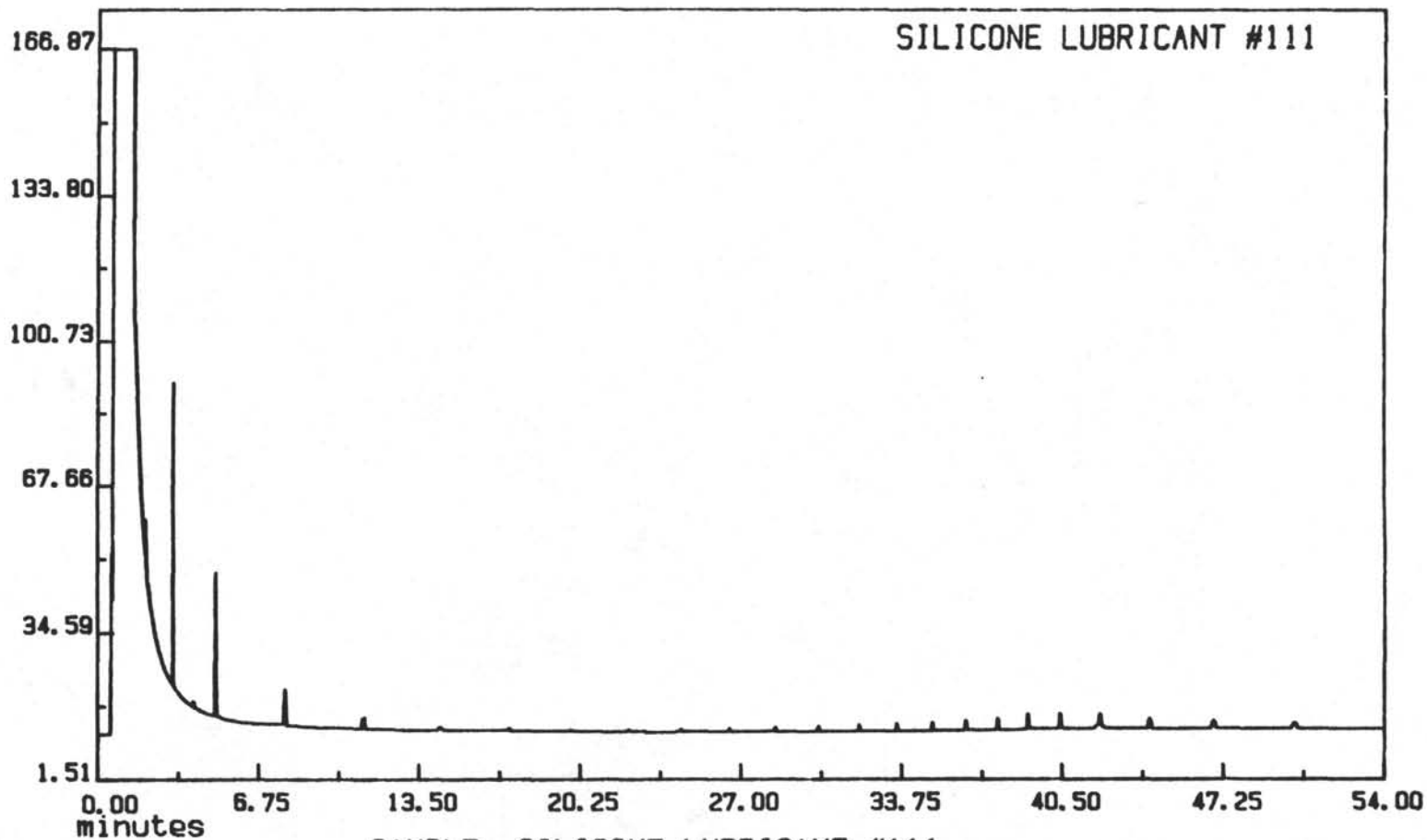
AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: BAKER-LOC
ANALYZED: Wed Jul 17, 1985 4:12:24 pm
RESULT: /DATA/LOOP/RESULT/CONT30.RES

Figure A-28. Gas chromatogram of Baker-Loc.

AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: SILICONE LUBRICANT #111
ANALYZED: Wed Jul 17, 1985 3:05:27 pm
RESULT: /DATA/LOOP/RESULT/CONT31.RES

Figure A-29. Gas chromatogram of Silicone Lubricant #111.

AMPLITUDE/1000 (Enlarged x 3.0)

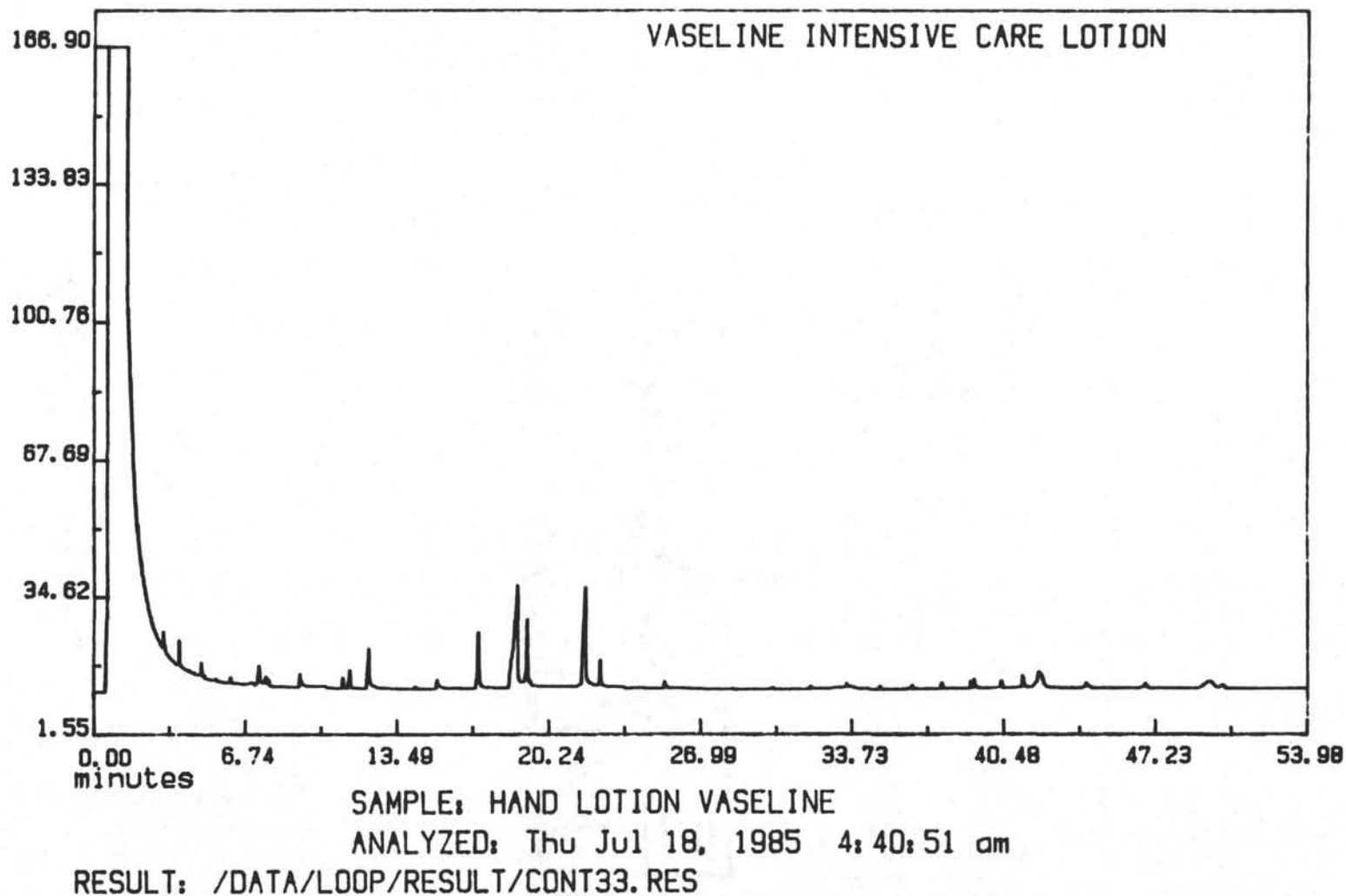
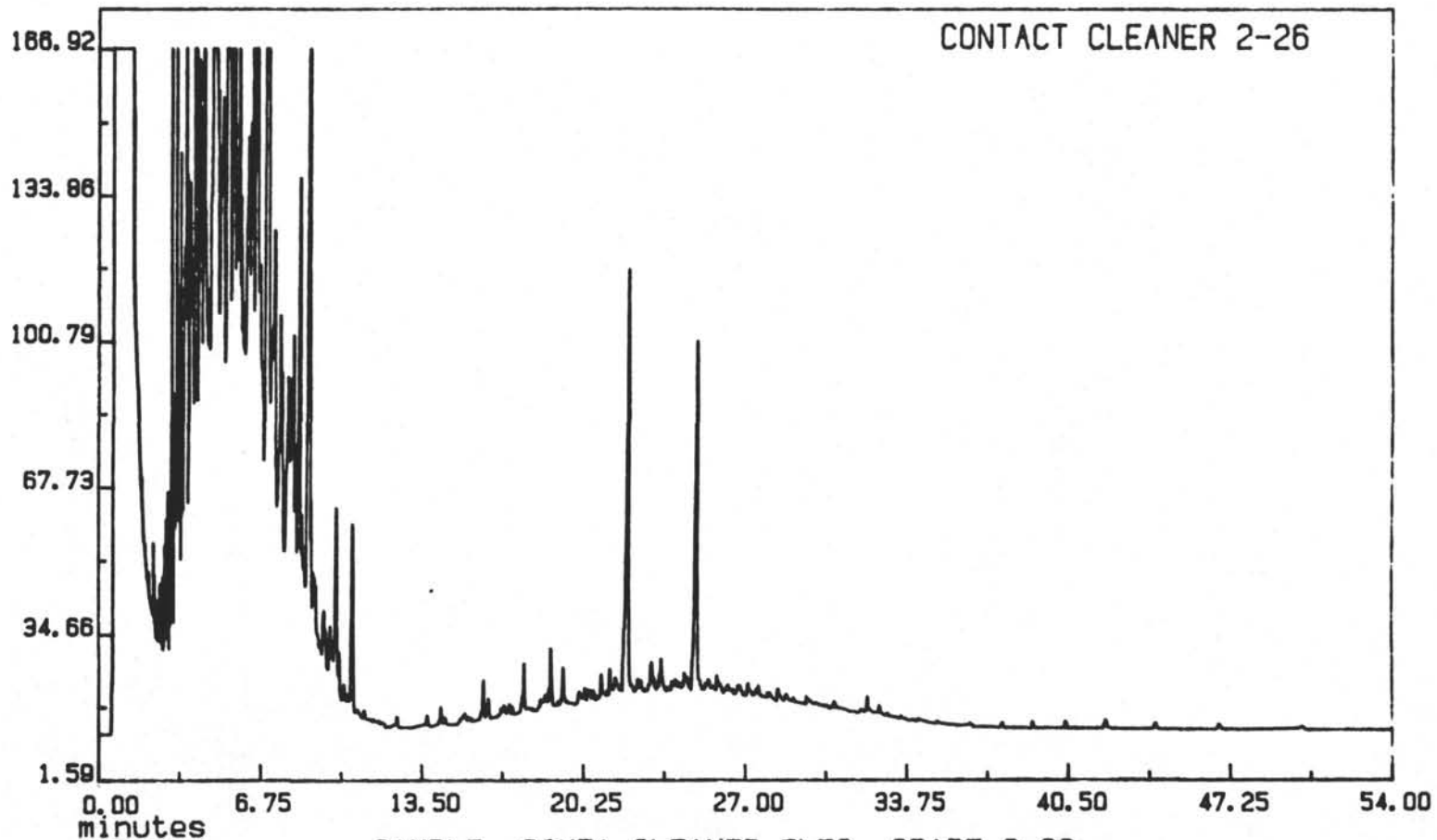


Figure A-30. Gas chromatogram of Vaseline Hand Lotion.

AMPLITUDE/1000 (Enlarged x 3.0)



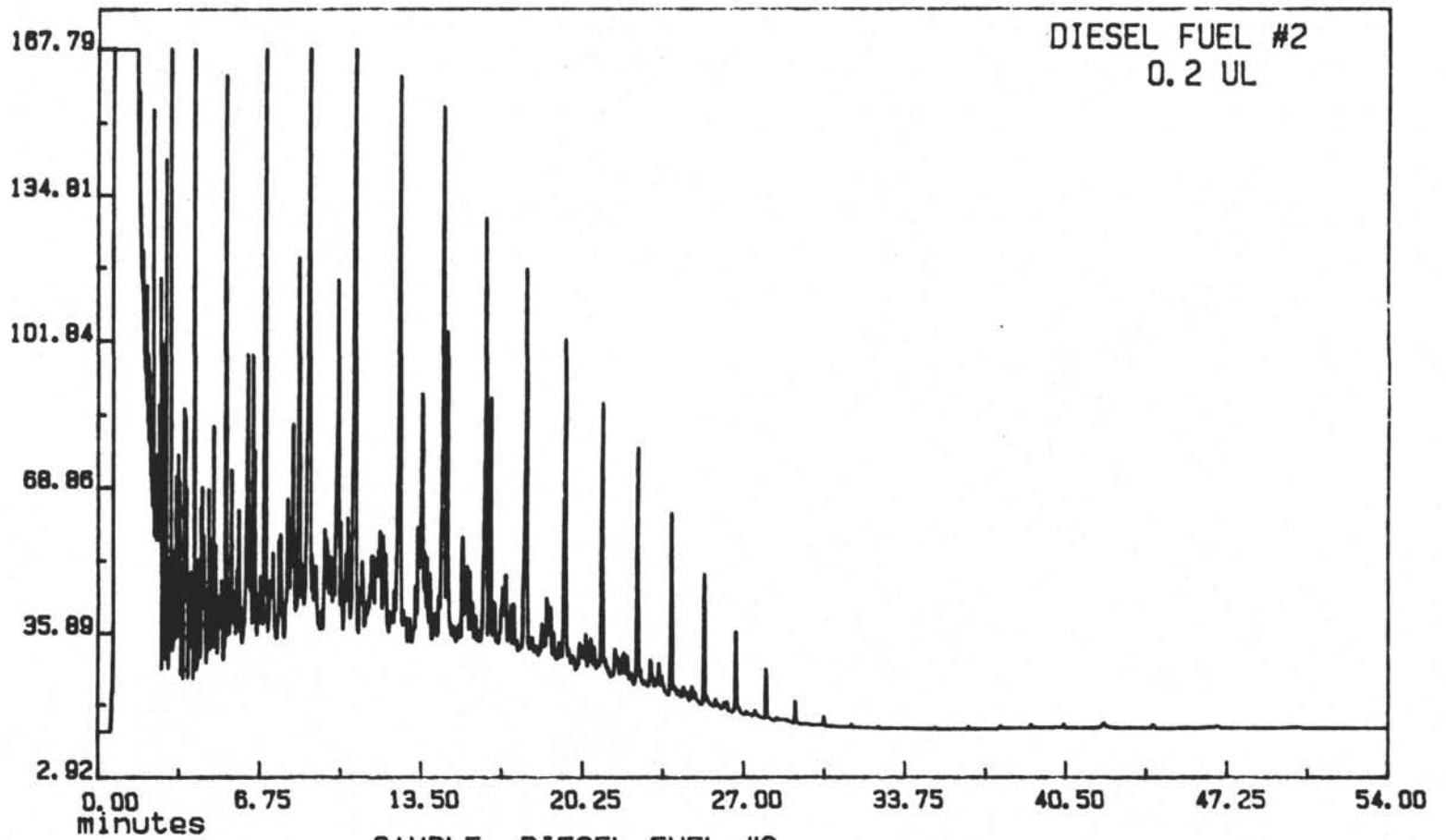
SAMPLE: CONTA CLEANER ELEC. GRADE 2-26

ANALYZED: Wed Jul 17, 1985 10:16:24 pm

RESULT: /DATA/LOOP/RESULT/CONT27.RES

Figure A-31. Gas chromatogram of Contact Cleaner Elec. Grade 2-26.

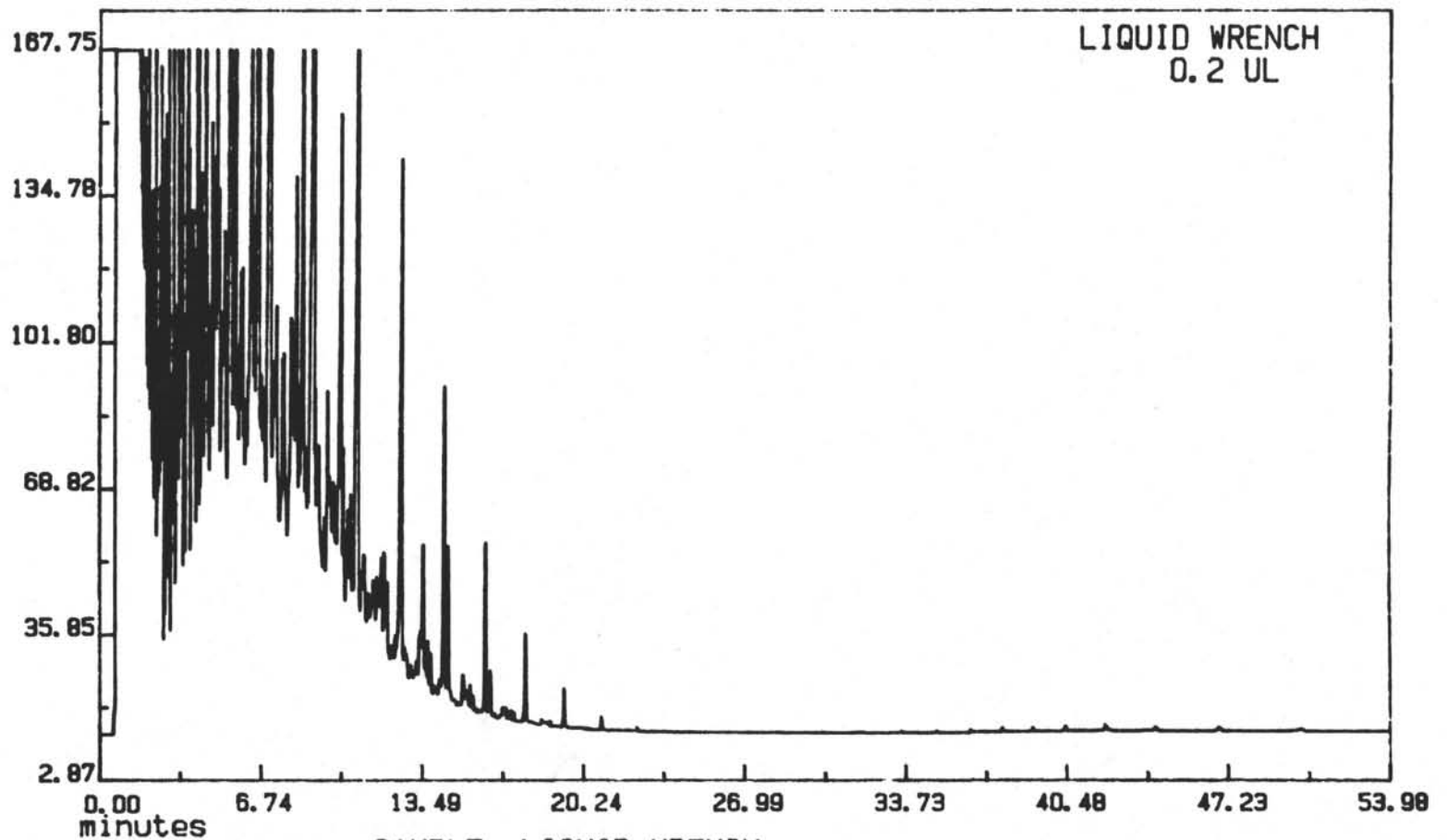
AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: DIESEL FUEL #2
ANALYZED: Wed Jul 24, 1985 4:55:56 am
RESULT: /DATA/LOOP/RESULT/CONT34R.RES

Figure A-32. Gas chromatogram of Diesel Fuel #2.

AMPLITUDE/1000 (Enlarged x 3.0)



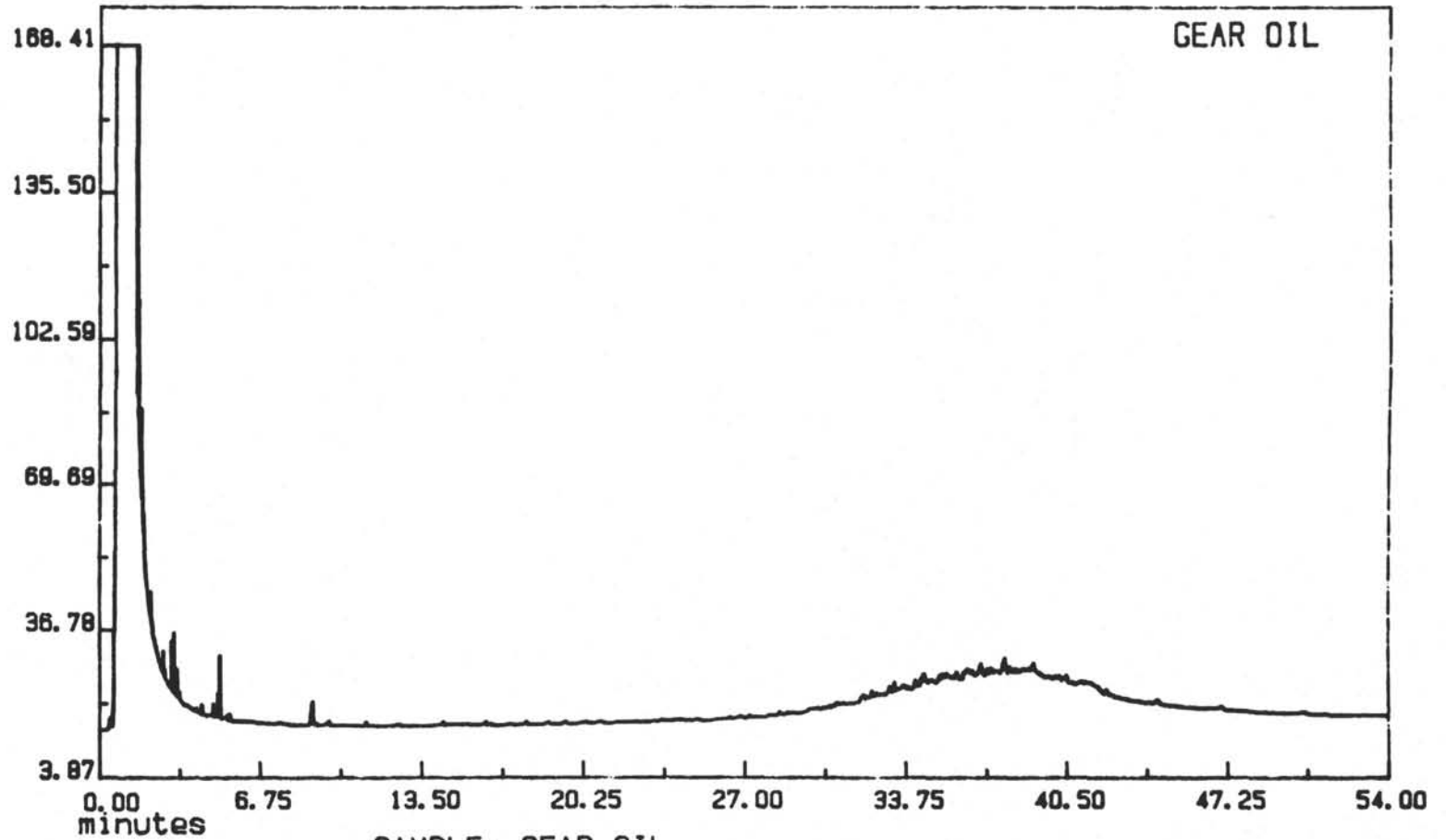
SAMPLE: LIQUID WRENCH

ANALYZED: Wed Jul 24, 1985 6:02:19 am

RESULT: /DATA/LOOP/RESULT/CONT24R.RES

Figure A-33. Gas chromatogram of Liquid Wrench.

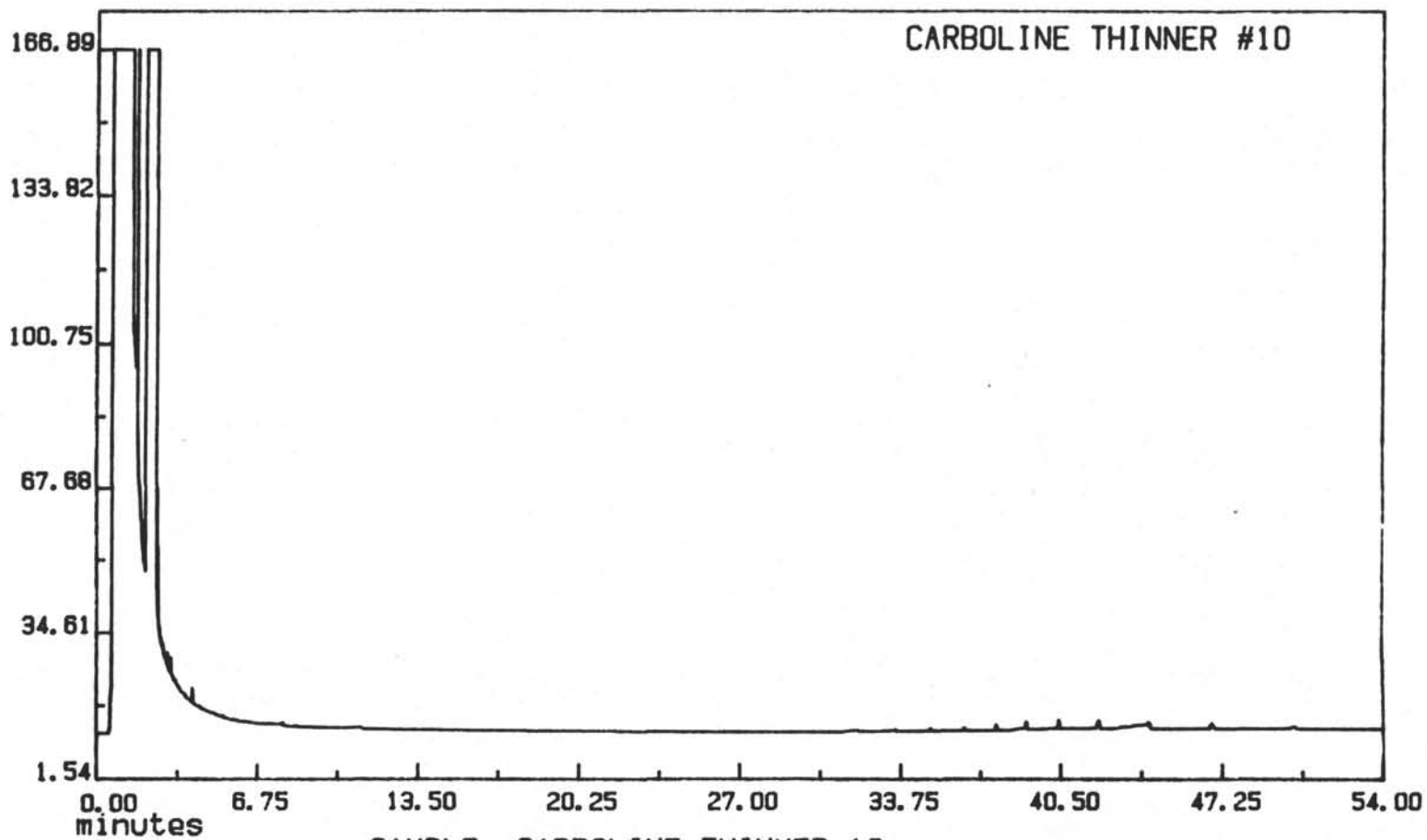
AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: GEAR OIL
ANALYZED: Fri Jul 19, 1985 9:35:30 pm
RESULT: /DATA/LOOP/RESULT/CONT37.RES

Figure A-34. Gas chromatogram of Gear Oil.

AMPLITUDE/1000 (Enlarged x 3.0)



SAMPLE: CARBOLINE THINNER 10
ANALYZED: Wed Jul 17, 1985 5:19:20 pm
RESULT: /DATA/LOOP/RESULT/CONT29.RES

Figure A-35. Gas chromatogram of Carboline Thinner 10.

AMPLITUDE/1000 (Enlarged x 3.0)

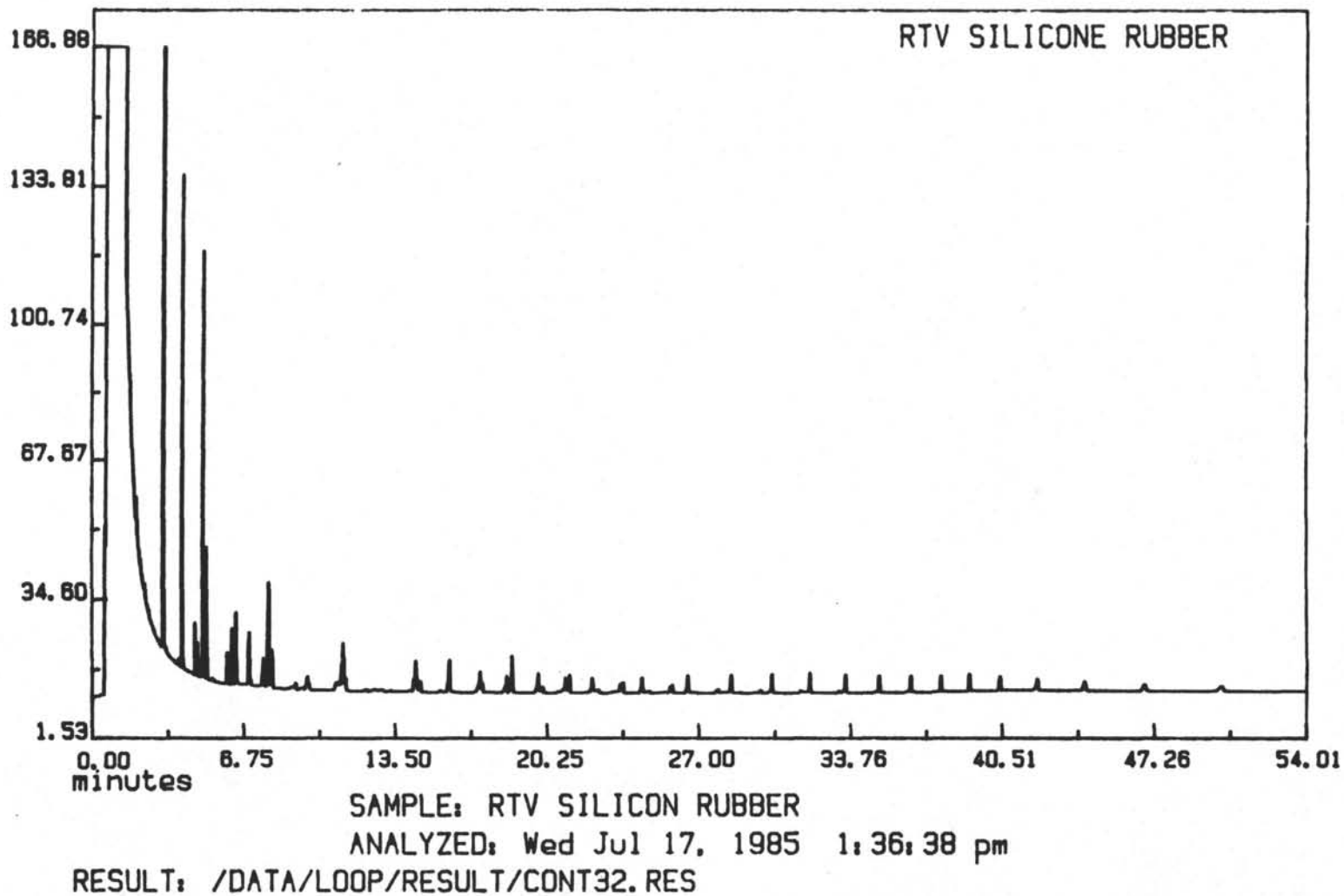


Figure A-36. Gas chromatogram of RTV Silicone Rubber.

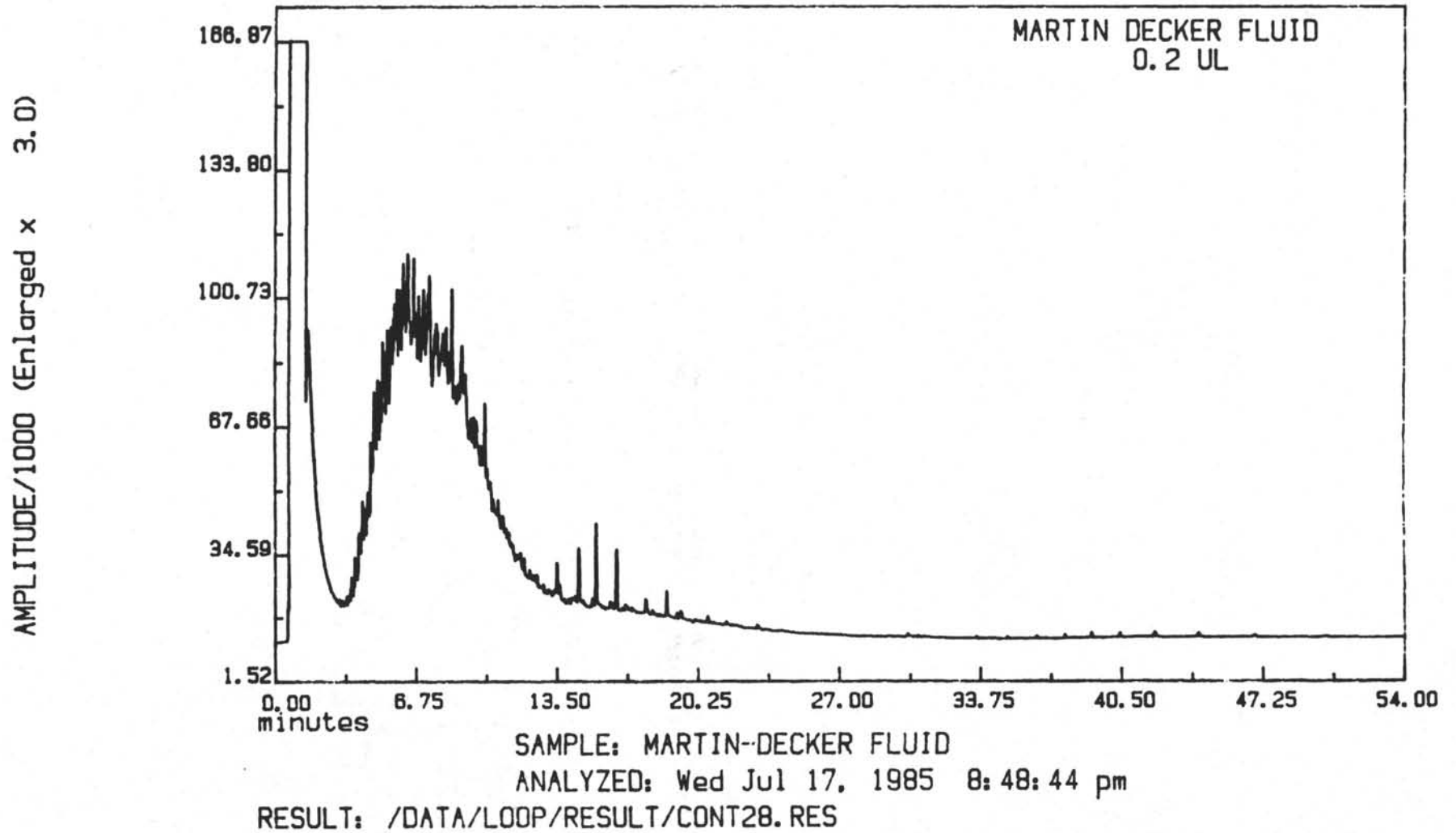


Figure A-37. Gas chromatogram of Martin-Decker Fluid.

APPENDIX B: PREPARATION OF VACUTAINERS FOR SHIPBOARD USE⁺

Introduction

Vacutainers, used for sampling gases escaping from sediment confined in core liners, have unacceptably high concentrations of hydrocarbon gases including methane and ethane. This hydrocarbon background can be reduced or removed by evacuating the vacutainers with the laboratory freeze-dryer for at least 10 min and using the vacutainers for sampling within about a 12 hr period. Preliminary evidence suggests that once a sample is taken, it can be stored without significant contamination by outgassing from the rubber stopper.

The vacutainer stopper should be sealed, however, with RTV Silicone Sealant to prevent sample loss.

The Problem

Gas escaping from sediment is often manifest as gas expansion cracks or voids developed while the sediment is confined in the core liner. The gas in these voids is sampled by means of vacutainers. The procedure involves a special tool consisting of a hollow point for penetrating the core liner, a valve to control the release of gas, and a needle to let the gas pass into a vacutainer. The procedure works well for collecting gas samples, but the vacutainers have a background of hydrocarbon gases which can interfere significantly in analyses especially when the core gas itself contains low amounts of hydrocarbons. In this paper we report a brief study of the hydrocarbon gases in vacutainers, and we describe a simple way to clean up the vacutainers so that they are acceptable for shipboard work.

Method

Vacutainers were selected randomly from Lot 4F093 (Exp. Date 07/15/86) supplied by B-D (Becton-Dickinson):

Vacutainer Brand

Evacuated Blood Collection Tube

Red Stopper, 20 ml, 165 x 16 mm

100 tubes per lot

Becton-Dickinson

Division of Becton, Dickinson and Co.

Rutherford, New Jersey 07070

⁺Keith A. Kvenvolden, U.S. Geological Survey, Menlo Park, CA 94025 and Thomas J. McDonald, Department of Oceanography, Texas A&M University, College Station, Texas 77843.

We tested various ways to remove the hydrocarbon background from the vacutainers. The H-P 5890A Gas Chromatograph with Option 820 (Natural Gas Analyzer) was used to detect and quantify the hydrocarbons. In all of our trials we employed the Labconco Freeze Dryer 8 as a vacuum source to remove hydrocarbons and to reestablish vacuum within the vacutainers. For this purpose we plugged a port of the freeze-dryer with a vacutainer stopper inserted backwards. A double ended 20G needle (B-D Vacutainer Needle) was used to connect the plugged port of the freeze-dryer to a vacutainer. In our first trials, we removed the stopper from the vacutainer and flushed the open tube with helium. The vacutainer was reassembled and evacuated with the freeze-dryer. By this method we found we could satisfactorily remove the hydrocarbons, but an alternate procedure worked just as well and was faster. In this alternate procedure, we simply took the vacutainer as supplied and attached it to the freeze-dryer. Evacuating for a period of 10 min or longer at about 8 microns Hg vacuum essentially removed the hydrocarbon gases.

Results and Discussion

Vacutainers as supplied by B-D have a vacuum of about 20 to 24 in. Hg. With the freeze-dryer, a vacuum of about 25 in. Hg could be established in the vacutainers. This latter vacuum could be detected with the Vacuum Leak Detector, commonly called a Tesla Coil, (for example, Thomas Scientific 9675-L10). In our survey of B-D vacutainers, we found that only about 3 of 20 vacutainers had sufficient vacuum to test positively (bluish glow in darkened room). When vacuum was reestablished in the vacutainers by means of the freeze-dryer, this vacuum gave a positive test with the vacuum leak detector. A vacuum gauge (for example, Alltech 8028) was used to measure the actual vacuum, but with each test the vacuum was reduced by about 2 in. Hg.

We found that the reestablished vacuum varied after a 24 hr period. In our tests the vacuums ranged from 20 to 24 in. Hg after 24 hr, but one vacutainer had atmospheric pressure. Because of this last result, we recommend that the vacutainers with reestablished vacuums be used within 12 hr and that the vacuums be checked with a leak detector or gauge immediately before use.

To test the hydrocarbon background in vacutainers, we added an atmosphere of helium to each vacutainer and removed 5 cc for injection into the gas chromatograph. Figures B-1 through B-5 illustrate by means of gas chromatograms the hydrocarbon background of the vacutainers and the reduction of this background by the procedures just described. Figure B-1 is a standard mixture of hydrocarbons and is for reference. Figure B-2 shows a typical hydrocarbon background in the vacutainers of the lot supplied by B-D. Methane, ethane, propane, and n-hexane are present in concentrations ranging from 5 to 113 ppm. An unknown is also present at concentrations comparable to methane. (This unknown has a retention time between i-butane and n-butane.) After the vacutainer was evacuated on the freeze-dryer, the hydrocarbon background was reduced (Fig. B-3) so that the only hydrocarbon detected was methane at 2 ppm. The unknown was also reduced significantly. Sometimes the hydrocarbon background was completely removed (Fig. B-4) and could not be distinguished from the helium blank (Fig. B-5). Thus by reestablishing the vacuum in

vacutainers, the hydrocarbon background, except for methane, cannot be detected. Methane can be reduced at least to 2 ppm and often to lower concentrations.

Upon storage for 24 hr of the vacutainers with reestablished vacuums, there appears to be an increase in the concentration of the unknown. Methane may also increase in amount, but as illustrated in the example on Figure B-6, the methane is present at less than 2 ppm. The source of the increasing compounds is likely the rubber stopper of the vacutainer. Because of the possibility of continued outgassing from the stopper during a 24 hr storage under vacuum, we recommend that the vacutainers be used within 12 hr of their preparation.

We also noted that if a prepared vacutainer was stored with an atmosphere of helium inside for 24 hr, there was no obvious increase in the amounts of background components. This preliminary observation suggests that the cleaned-up vacutainers can be used for long-term storage. For this purpose we recommend that RTV Silicone Sealant be used to coat the stopper where needle penetrations have been made. The use of these prepared vacutainers for long-term storage should be investigated further before committing them for this purpose. For sample collection, however, the cleaned-up vacutainers appear to be adequate if precautions are taken to use the vacutainers soon after the clean-up procedure.

Summary

The hydrocarbon background of shipboard B-D vacutainers can be reduced significantly and in most cases below detection limits by simply evacuating the vacutainer on the laboratory freeze-dryer for at least 10 min. The vacuum can be checked with a vacuum leak detector or vacuum gauge which should read about 25 in. Hg. It is recommended that the vacutainers be used within 12 hr of preparation in order to assure that no new hydrocarbons have outgassed from the rubber stopper. The use of these prepared vacutainers for long-term sample storage needs to be investigated further.

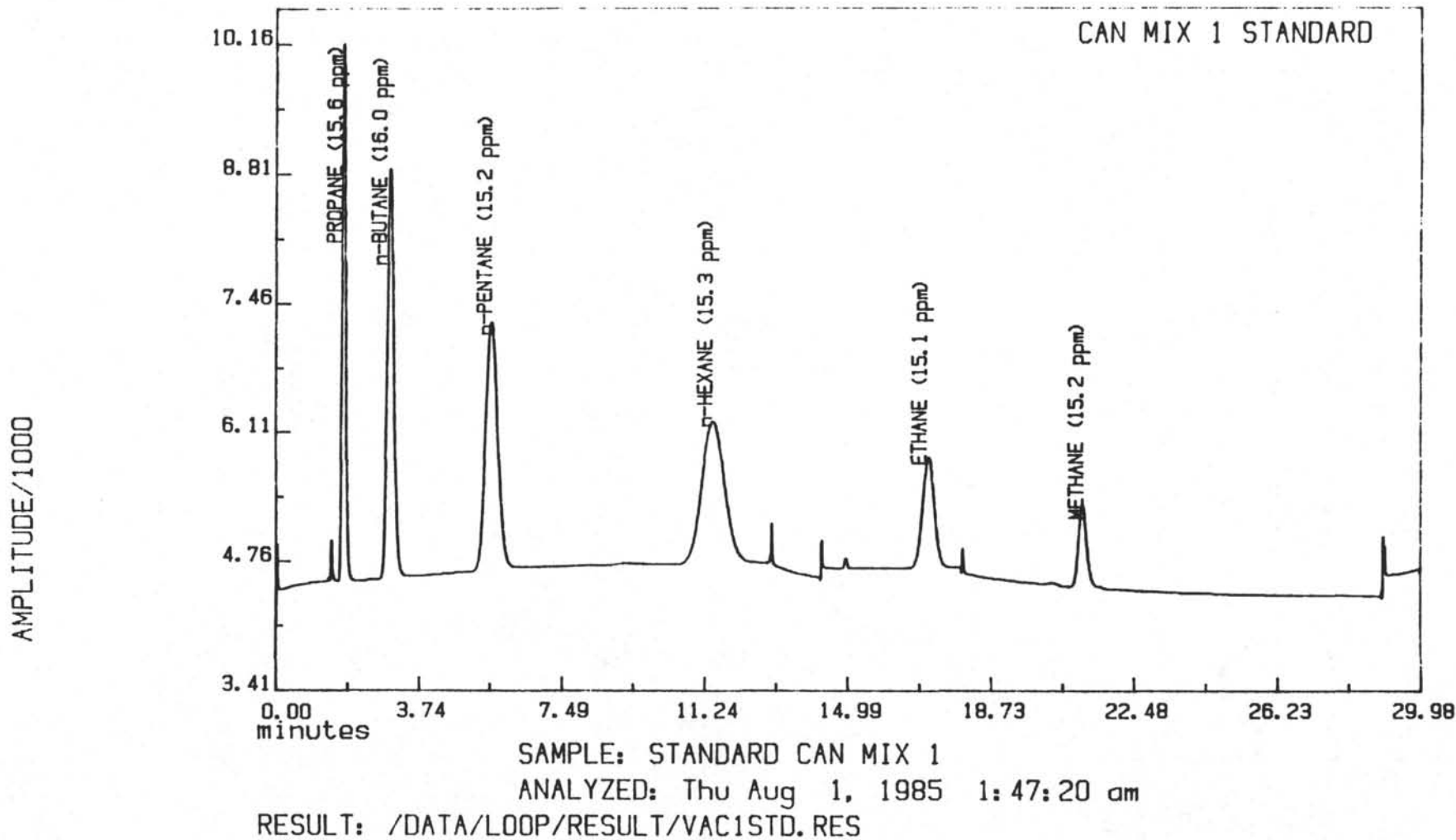


Figure B-1. Gas chromatogram of a standard mixture of hydrocarbons.

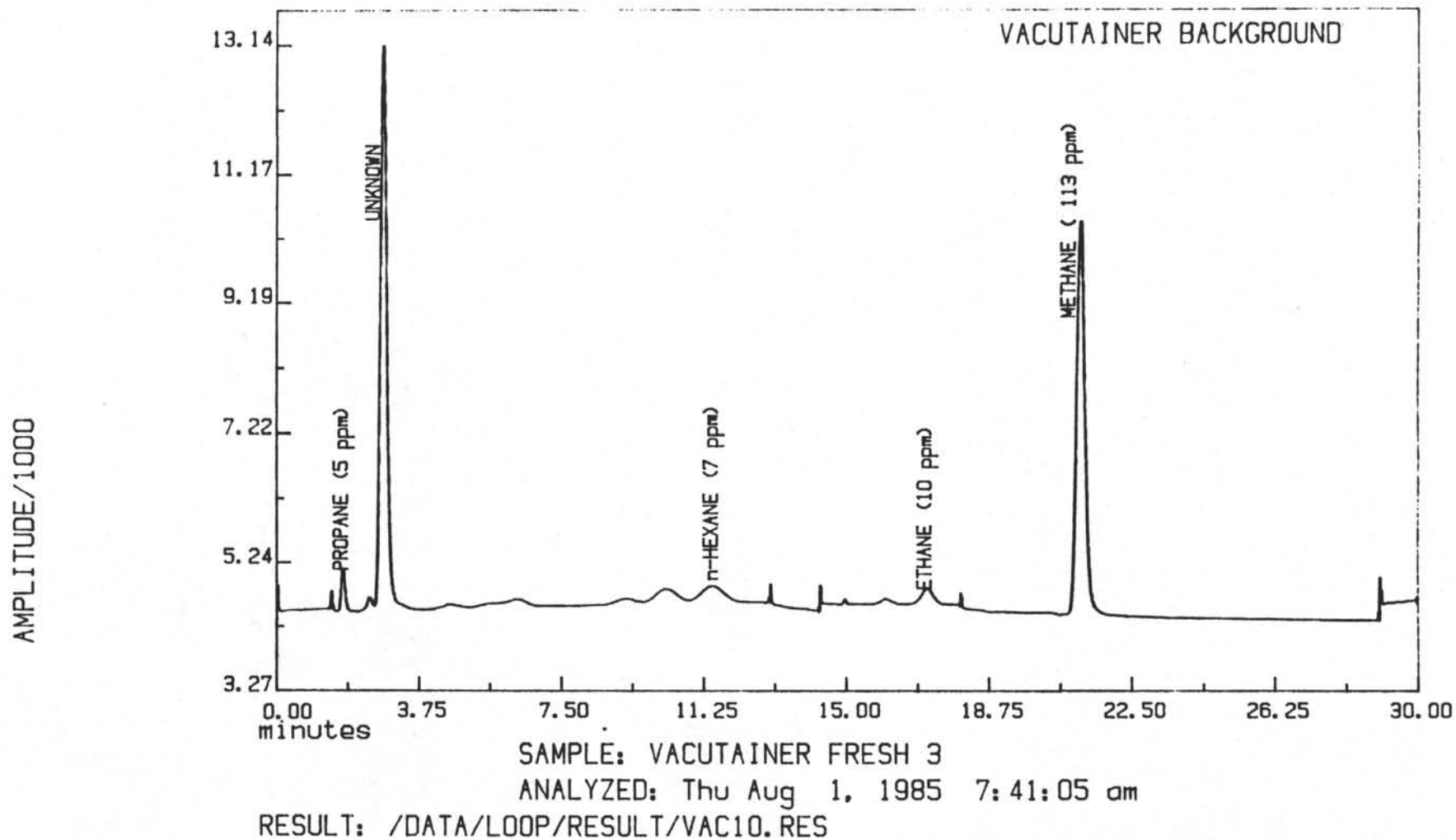
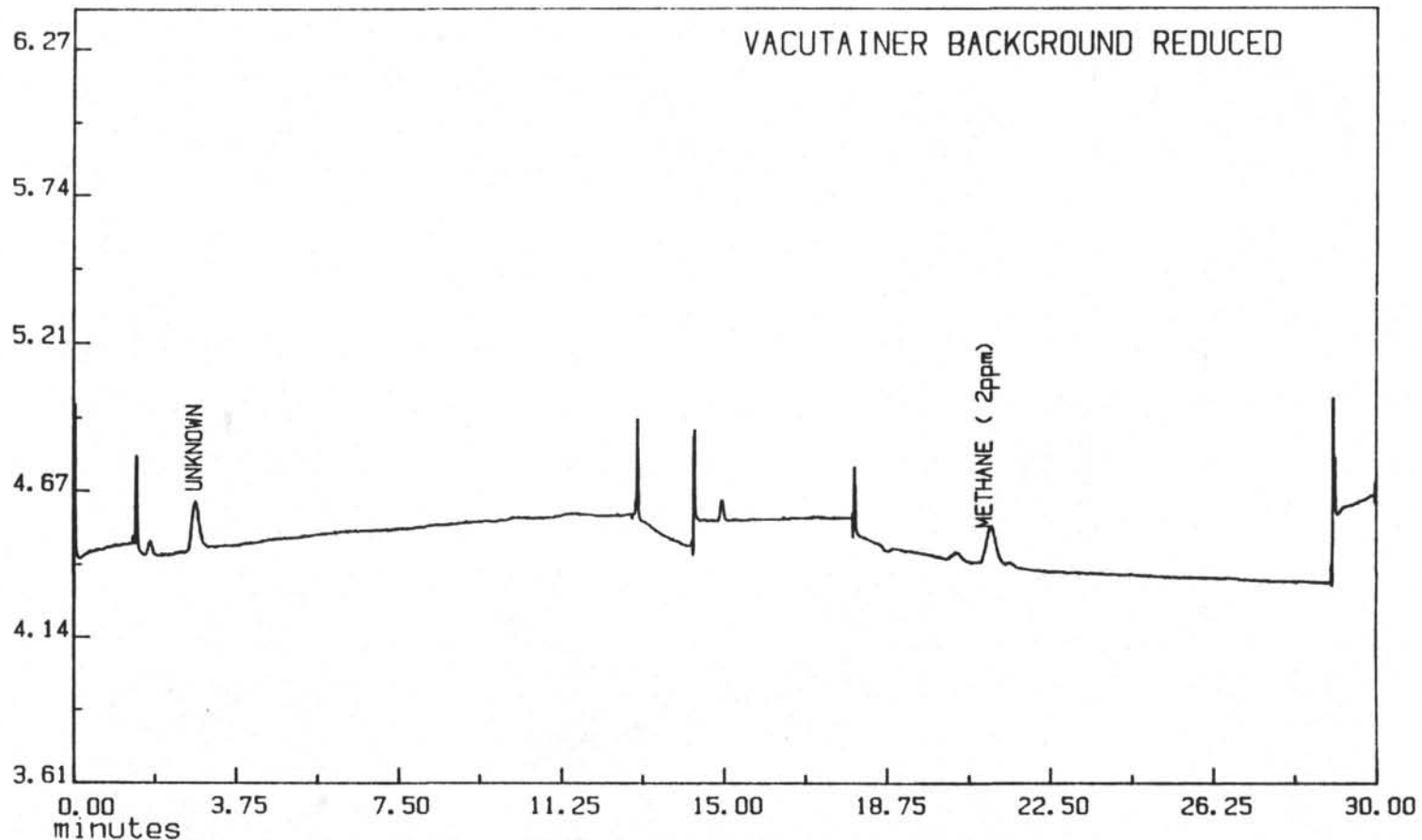


Figure B-2. Gas chromatogram showing a typical hydrocarbon background in the vacutainers.

AMPLITUDE/1000 (Enlarged x .5)



SAMPLE: VACUTAINER FRESH 3 EVACUATED
ANALYZED: Thu Aug 1, 1985 8:20:58 am
RESULT: /DATA/LOOP/RESULT/VAC11.RES

Figure B-3. Gas chromatogram showing the hydrocarbon background after the vacutainer was evacuated on the freeze dryer.

AMPLITUDE/1000 (Enlarged x .5)

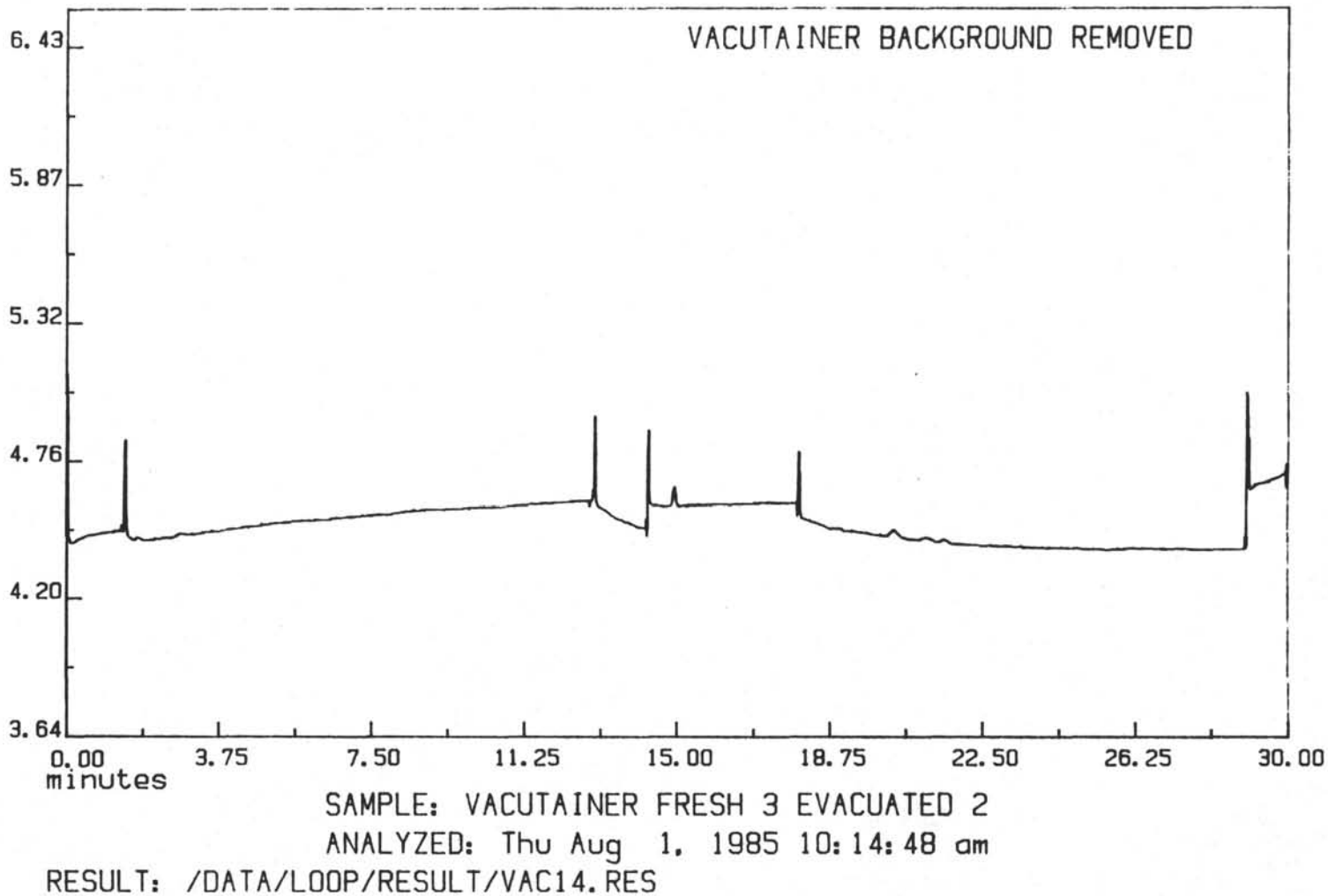


Figure B-4. Gas chromatogram with the hydrocarbon background completely removed.

AMPLITUDE/1000 (Enlarged x .5)

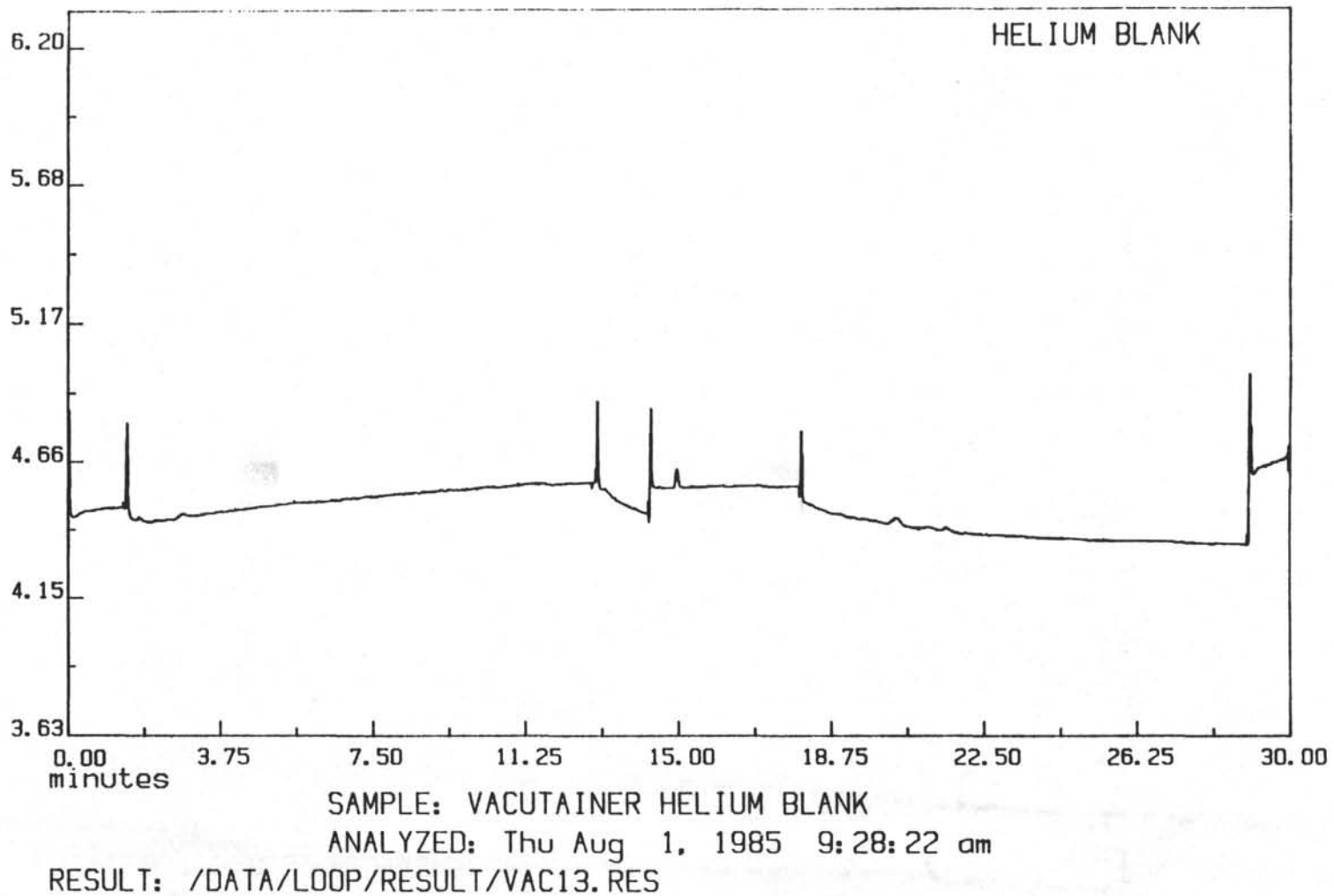


Figure B-5. Gas chromatogram of a helium blank.

AMPLITUDE/1000 (Enlarged x .5)

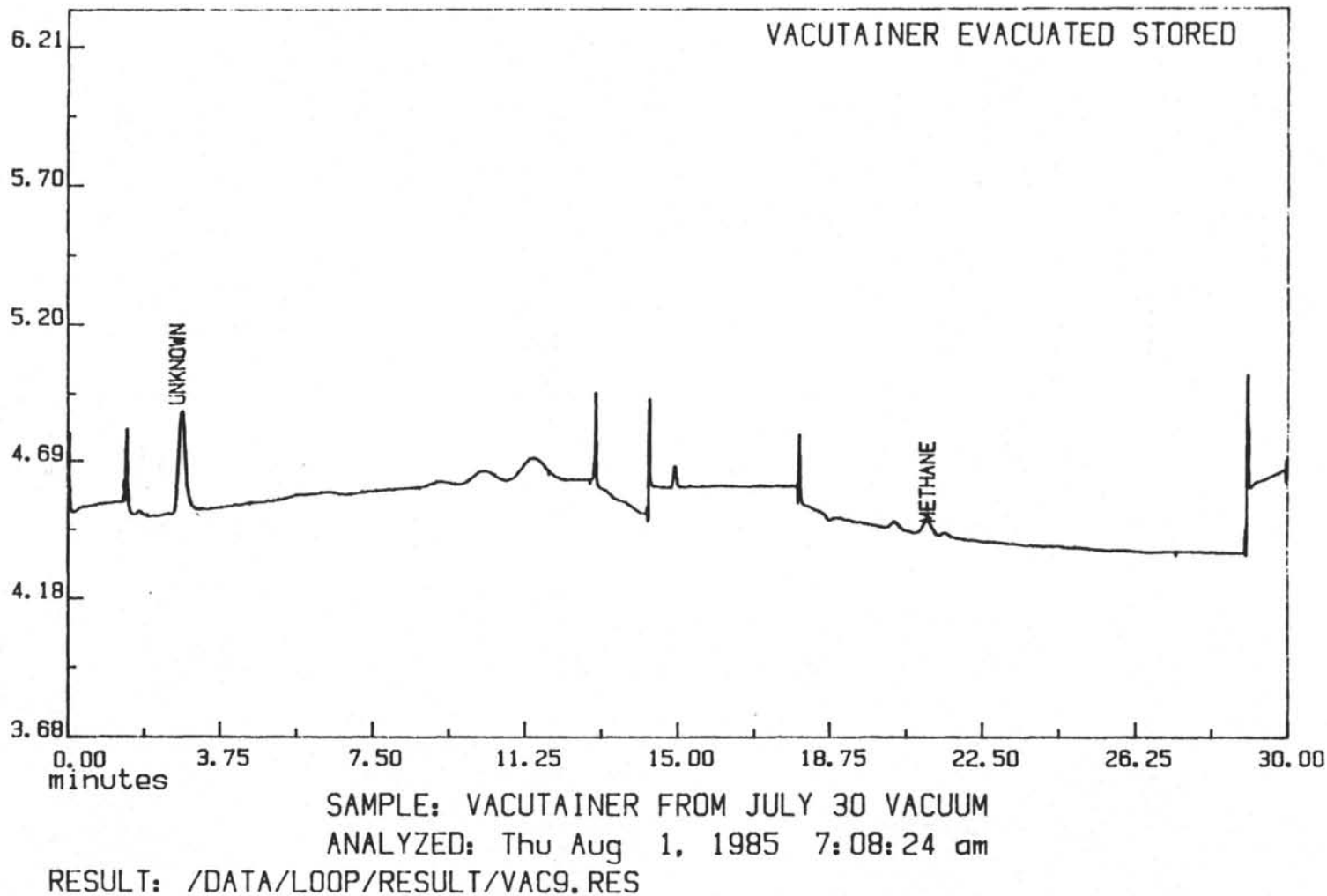


Figure B-6. Gas chromatogram showing a hydrocarbon background upon 24 hour storage of a vacutainer with reestablished vacuums.