

A STUDY OF THE AROMATIC  
FRACTION OF OIL SHALES AND  
OTHER CARBONACEOUS DEPOSITS FROM THE  
GREEN RIVER FORMATION IN UTAH

FARHAD BAKHSANDEH

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirement for the degree of Master of Science in Chemistry.

Signed: Farhad Bakshandeh

Golden, Colorado

Date: 2/11 1977

Approved: George H. Kennedy  
Thesis Advisor

George H. Kennedy  
Head of Department

Golden, Colorado

Date: 2/11 1977

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## ABSTRACT

Four tar sand outcrop samples, including ones from Raven Ridge, White Rocks, P. R. Spring and Sunny Side, a sample of gilsonite, a sample of Red Wash oil, a sample of the Mahogany Marker and a sample of oil shale, all from the Green River Formation, were studied for clues to their origin.

The bitumens of the above samples were separated by liquid adsorption chromatography into the following fractions: Saturated hydrocarbons; aromatic hydrocarbons; asphaltenes, and a fraction remaining on the column. For the first five samples the silica gel adsorbant was subjected to a new pretreatment method which improved the separation of the saturated hydrocarbons from the aromatics. The hydrocarbon fractions were also subjected to gas-liquid chromatographic analysis.

The similarities of the saturated and aromatic hydrocarbon fractions of the tar sand samples suggest a common origin for them.

A comparison of the aromatic hydrocarbon fractions of the different samples indicates that oil shale or Mahogany Marker bitumen (which has not migrated), may be the source of all of the other samples except Red Wash oil, which must have had a different origin.

## TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES . . . . .	VI
LIST OF TABLES . . . . .	VIII
ACKNOWLEDGEMENTS . . . . .	IX
INTRODUCTION. . . . .	1
THE ORIGIN OF THE GREEN RIVER FORMATION . . . . .	15
EXPERIMENTAL . . . . .	18
Samples . . . . .	18
Preparation of Reagents . . . . .	19
The New Method of Pretreatment of Silica Gel . . . . .	20
Extraction of the Bitumens . . . . .	20
Liquid-Adsorption Chromatography . . . . .	20
Gas-Liquid Chromatography. . . . .	23
Infrared Spectrometry. . . . .	28
DISCUSSION . . . . .	30
Advantages and Disadvantages of the New Method of Pretreatment of Silica Gel . . . . .	30
Bitumens Analysis. . . . .	33
The Relations of the Samples Drawn from L.A.C. . . . .	33
The Relations Among the Samples Drawn from G.L.C. . . . .	35
Infrared Analysis Relations Among the Samples . . . . .	41
CONCLUSIONS . . . . .	42

Table of Contents - Continued

Page

APPENDIX - CHROMATOGRAMS . . . . .	45
REFERENCES . . . . .	66

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## List of Figures - Continued

<u>Figure</u>		<u>Page</u>
12-A	Chromatogram of the aromatic fraction of gilsonite . . . . . (Silica gel was pretreated with concentrated nitric acid)	56
13	Chromatogram of the aromatic fraction of Mahogany Marker oil shale. . . . .	57
14	Chromatogram of the aromatic fraction of Green River shale, SGR-1, U.S.G.S. . . . .	58
15	Chromatogram of the aromatic fraction of Red Wash crude oil (lighter fraction) . . . . .	59
16	Infrared of the aromatic fraction of gilsonite . . . . .	60
17	Infrared spectrum of carbontetra chloride . . . . .	61
18	Infrared spectrum of the aromatic fraction of Raven Ridge tarsand outcrop. . . . .	62
19	Infrared spectrum of the aromatic fraction of White Rocks tarsand outcrop . . . . .	63
20	Infrared spectrum of the aromatic fraction of P. R. Spring tarsand outcrop . . . . .	64
21	Infrared spectrum of the aromatic fraction of Sunny Side tarsand outcrop . . . . .	65

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## LIST OF TABLES

<u>Table</u>	<u>Page</u>
I The formation of the investigation area . . . . .	6
II Yield of bitumen obtained by extraction with normal hexane. . . . .	23
III The required amount of solvent for each cut . . .	24
IV The yield of the fractions, liquid adsorption chromatography on silica gel. . . . .	25
V The yield of the fractions, liquid adsorption chromatography on silica gel. . . . .	26
VI The ratio of the unsaturated to saturated CH in the aromatic fraction . . . . .	29
VII Parent molecular ions in $C_{28}H_{44}$ and $C_{29}H_{46}$ . . .	39
VIII The mass spectral data of the mixture of $C_{27}H_{42}$ , $C_{28}H_{44}$ , and $C_{29}H_{46}$ . . . . .	40

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## INTRODUCTION

The largest reservoirs of oil bearing shale in the United States are in the Green River Formation of Eocene age (50-60 million years) in Colorado, Utah, and Wyoming with the potential of two trillion barrels (Donnell, et al, 1967).

Most of the crude oil reservoirs of the world were deposited under marine condition, but the oil shales of the Green River Formation were deposited in Lacustrine or lake sediments (Oil and Gas Journal, March 9, 1964). The lake sediments with inter-fingering river deposits made up the Green River Shales with 1,500 to 2,000 feet thickness.

There were three lakes at the time of the Green River deposition:

- 1) Uinta (or Uintah) Lake in Utah and Colorado. It was the largest lake and occupied two basins, Utah's Uinta, and Colorado's Piceance Creek. According to John R. Donnell, et al (1967), the average area of the Utah lake was about 2,500 square miles and that of the Colorado lake was 500 square miles.
- 2) Gosiute Lake in Wyoming.
- 3) Unnamed lake which was located in the smaller basin area (fossil syncline) of very western Wyoming (Figure I).

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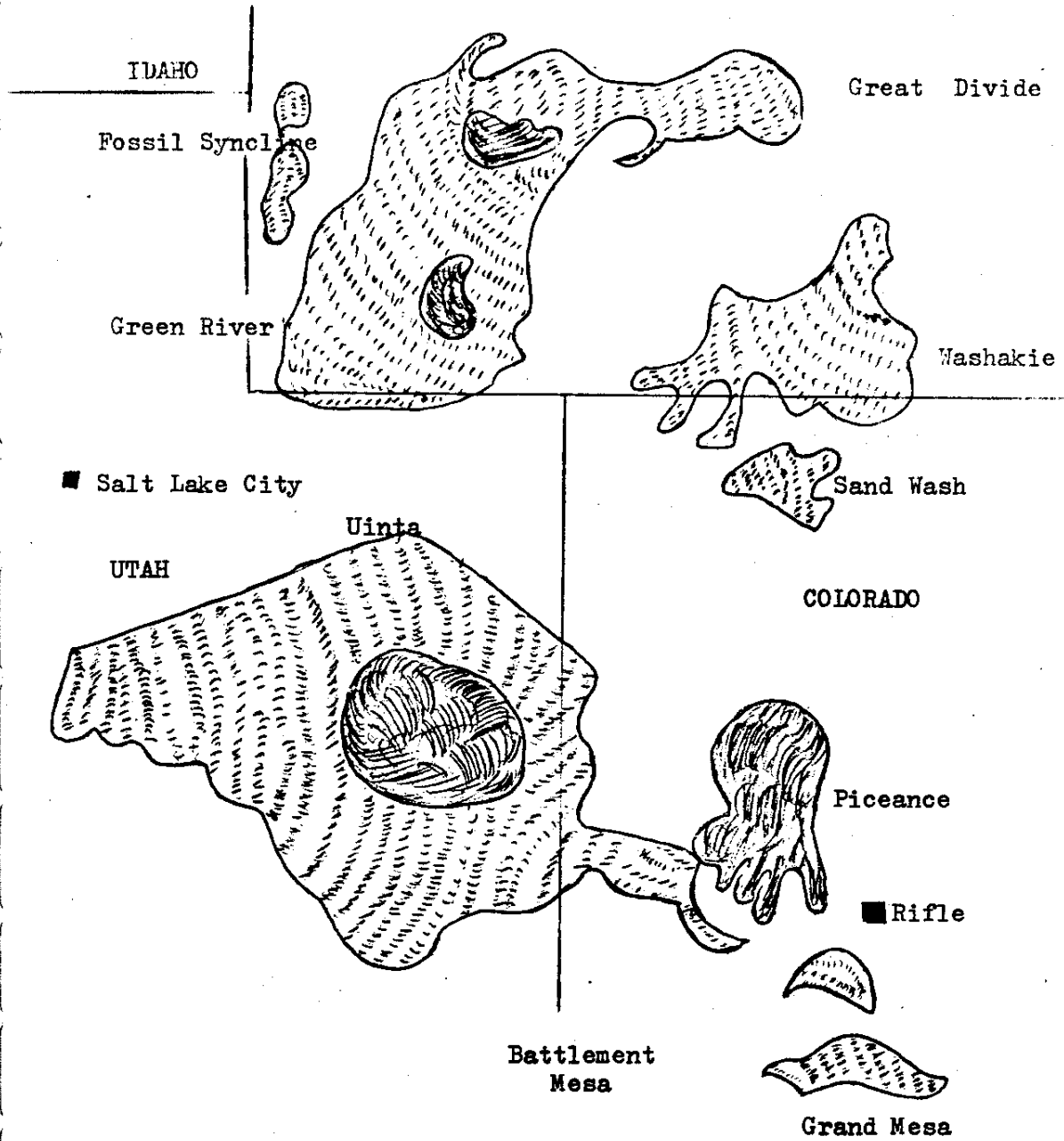


FIGURE I: The biggest undeveloped oil reserve in the world: The Green River Oil Shales of COLO., Utah, and Wyoming.

The oil shale in the Green River Formation was formed in lake Uinta, in Colorado and Utah, and Lake Gosiute in Wyoming. These two lakes expanded and joined together forming one big lake which was called Lake Uinta. This episode occurred after deposition of the saline minerals in the Piceance Creek Basin. During the Eocene, the Uinta-Piceance Creek Basin was subsiding and filling up with sediments stripped from the Uinta Mountains.

The areas from which the samples in this investigation were taken (Figure 2), are White Rocks, Raven Ridge, P. R. Spring, Red Wash, and Sunnyside which are surrounded by the Strawberry Reservoir on the west, the Utah-Colorado border on the east, the Uinta Mountains on the north, and the Book Cliffs on the south.

According to Thompson and Williamson (1973) some positive structural elements were formed during the Laramide Orogeny and later structural episodes which were:

- 1) The east-west trending Uinta Mountains.
- 2) The north-south trending Wasatch Mountains and Douglas Creek Arch which deformed the earlier (Permian) San Rafael swell during the Laramide Orogeny.
- 3) During the Pennsylvanian, the Uncompahgre became a positive element.

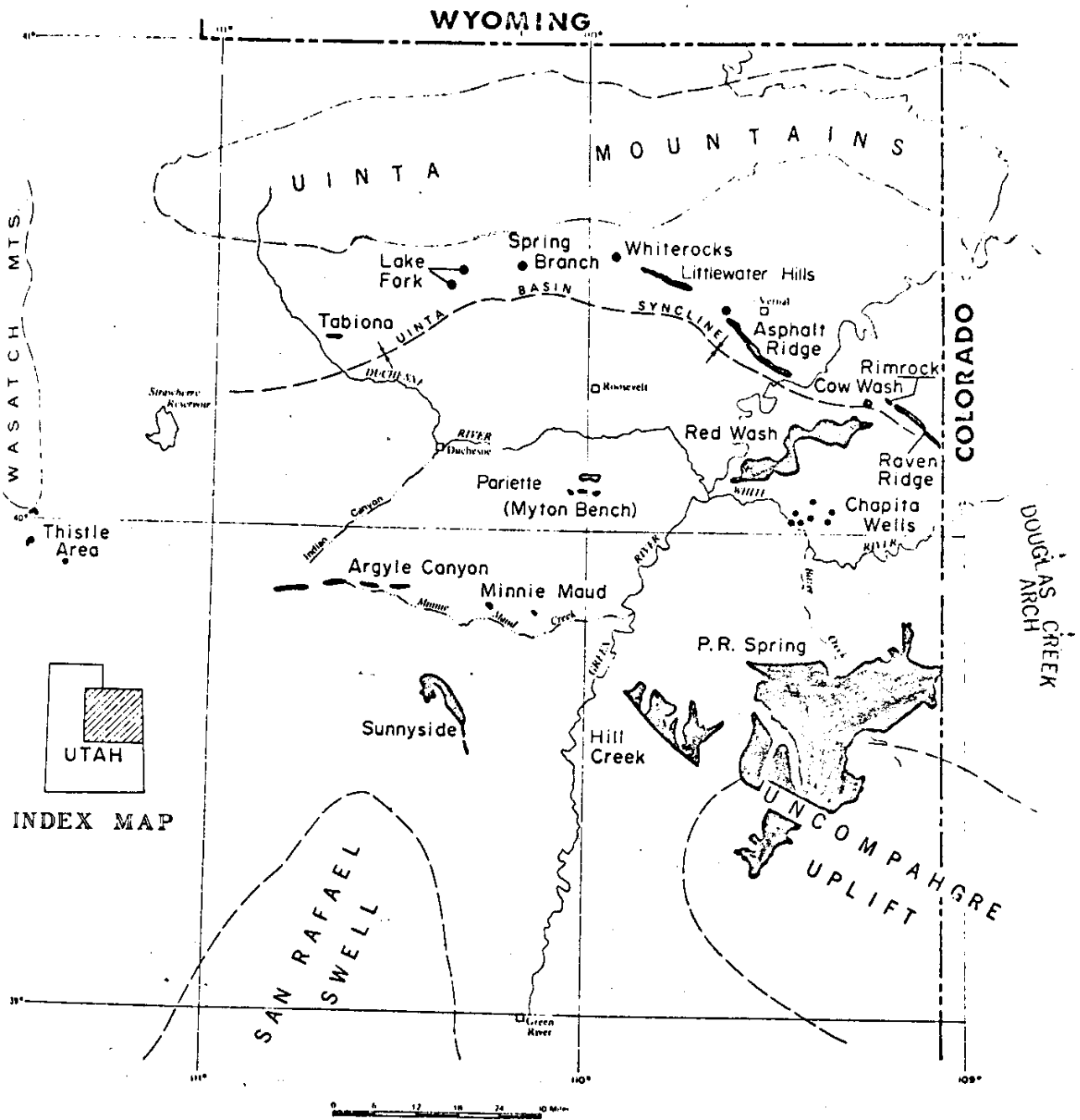


Figure 2: The map Of Uinta Basin showing positive areas, oil-impregnated sandstone deposits(black patterns),geographic localities and area of study.

(From Thompson and Williamson, 1973)

All of these structural features enclosed the sharply asymmetrical Uinta Basin syncline and furnished sediment to Lake Uinta in Utah during deposition of the black shale facies. The formation of the investigation area in which oil impregnation occurred is shown in Table I.

More petroleum is believed to be in the black shale facies of the Green River Formation than any other Lacustrine facies. This facies contains the oldest rocks assigned to the Green River Formation in the Uinta Basin of Utah. The facies are also older than other beds of Green River origin in Wyoming and Colorado.

Gilsonite veins, which are essentially vertical, are as much as eighteen feet wide in massive sandstone beds of the Uinta Formation and of the shore facies of the Green River Formation.

About two trillion barrels of oil are contained in the three-state area in shales with thickness of 2,000 feet with averages of fifteen gallons per ton based on assays from the center, surface, and cores samples of the basins.

This investigation is a study of the aromatic fractions of the non-oil shale and the oil shale of the Green River Formation and comparison between them.

Understanding the origin and the relation between the hydrocarbons in ancient and recent sediments has been one of the most

DEPOSIT	FORMATION IN WHICH OIL IMPREGNATION OCCURS
P. R. SPRING	GREEN RIVER FORMATION "EO CENE"
SUNNY SIDE	WASATCH-GREEN RIVER FORMATION
WHITE ROCKS	NUGGET S <sub>s</sub> "JURASSIC ?"
RAVEN RIDGE	GREEN RIVER FORMATION "EOCENE"

Table I. THE FORMATION OF THE INVESTIGATION  
AREA.

interesting topics in organic geochemistry. Only a few years ago, the major problems were: separation, isolation, and identification of the hydrocarbons because of lack of adequate techniques and instruments. But today, with gas chromatographic (GC), ultra violet (UV), infrared (IR), nuclear magnetic resonance (NMR), and mass spectrometric techniques we can at least show the composition of the hydrocarbons. However, it is still difficult to understand the exact processes of their migrations between recent and ancient sediments because of many geologic variables.

Considerable work has been reported on the identification of aliphatic and aromatic compounds in petroleum and other sedimentary rocks (Bonilla's, 1973), but little has been done towards the identification of aromatic hydrocarbons in Green River shale and there is no report for the non(oil shale)deposits.

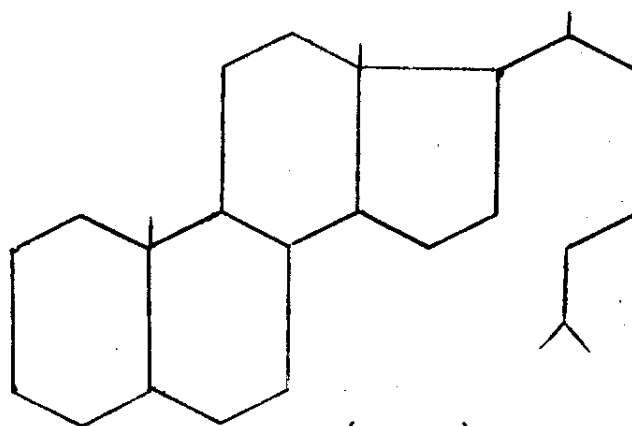
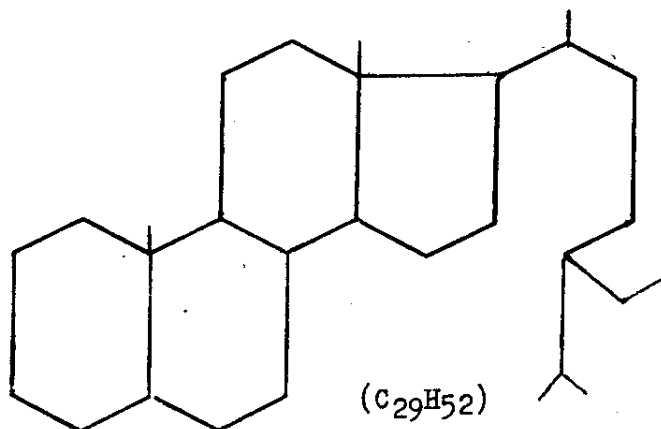
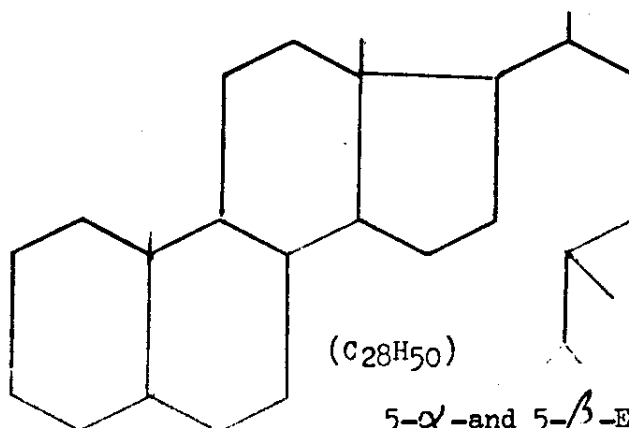
Robinson (1964) reported the uneven distribution of n-alkanes and the presence of large proportions of C<sub>16</sub>-, C<sub>18</sub>-, C<sub>19</sub>- (pristane), and C<sub>20</sub>- (phytane) isoprenoid alkanes. Burlingame et al (1965) reported the analytical isolation and identification of C<sub>27</sub>-, C<sub>28</sub>-, and C<sub>29</sub>- sterane and pentacyclic triterpane (C<sub>30</sub>H<sub>52</sub>).

Eglinton et al (1968) isolated 5- $\beta$ - and 5- $\alpha$  cholestane

( $C_{27}H_{48}$ ), and a stigmastane isomer ( $C_{29}H_{52}$ ) which was confirmed by Anders et al in 1969. They also identified two ambreanes ( $C_{30}H_{56}$ ), ergostane ( $C_{28}H_{50}$ ), and hopane ( $C_{30}H_{52}$ ), pentacyclic nortriterpane ( $C_{29}H_{50}$ ), pentacyclic triterpane ( $C_{31}H_{54}$ ). Gallegos (1971) and Anders and Robinson (1971) reported 48 and 22 additional compounds, respectively, in the bitumen of Green River Shale including other perhydro carotenes, steranes, terpanes, branched-paraffins, all of which seem to be related structurally to natural occurring isoprenoid lipids. Their structures are shown in Figure 3A.

There have been two reports published about the aromatic compounds in Green River shale so far. Gallegos (1973) reported phenyl cycloparaffin alkanes and other mono aromatics in Green River shale. The compounds he found were: Phenyl (cyclohexy) alkanes  $C_{16}H_{24}$ ,  $C_{17}H_{26}$  isomers,  $C_{18}H_{28}$ ,  $C_{19}H_{30}$ ,  $C_{20}H_{32}$ ,  $C_{21}H_{34}$ ,  $C_{22}H_{36}$ , and  $C_{26}H_{44}$  were about 55% of the shale; Benzomonocyclic paraffins  $C_{17}H_{24}$ ,  $C_{18}H_{26}$ , two isomers, and 12%; Alkylbenzenes  $C_{15}H_{24}$  and  $C_{18}H_{30}$ , two isomers, and 17%; Indan alkane  $C_{20}H_{30}$  and  $C_{21}H_{32}$  about 2%; Benzotricyclo paraffin  $C_{22}H_{32}$  and Naphthalene Cycloparaffin  $C_{21}H_{28}$ , which is the only dinuclear aromatic, both are less than 1% of the shale.

Anders (1973) reported more aromatic compounds (over

(C<sub>27</sub>H<sub>48</sub>)5- $\alpha$ -and 5- $\beta$ -Cholestane(C<sub>29</sub>H<sub>52</sub>)5- $\alpha$ -and 5- $\beta$ -Stigmastane(C<sub>28</sub>H<sub>50</sub>)5- $\alpha$ -and 5- $\beta$ -Ergostane

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FIGURE 3A. Some structures of the saturated hydrocarbons in the bitumen of Green River Shale.

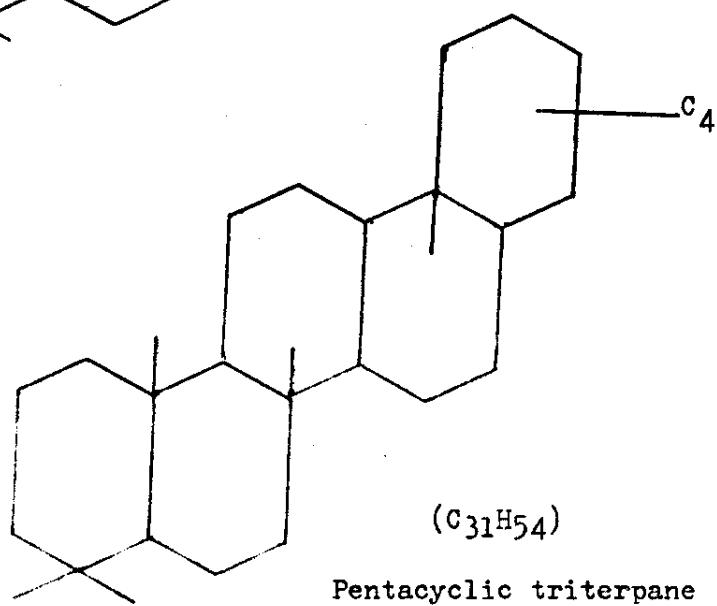
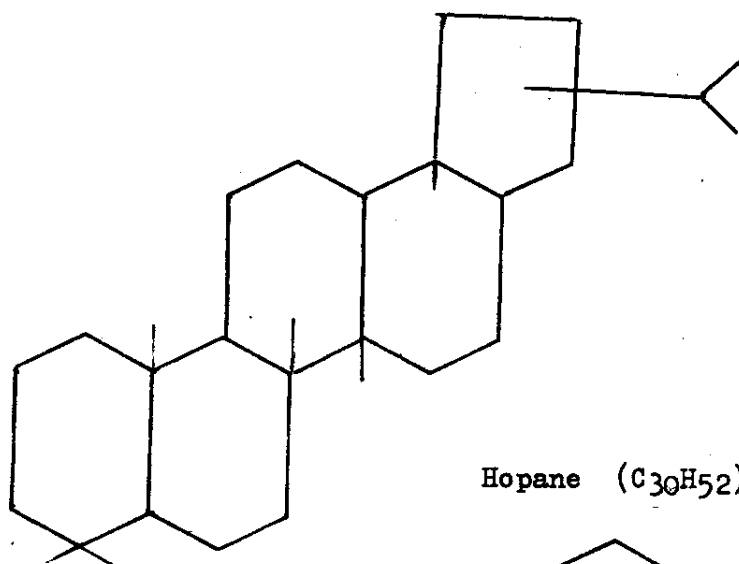
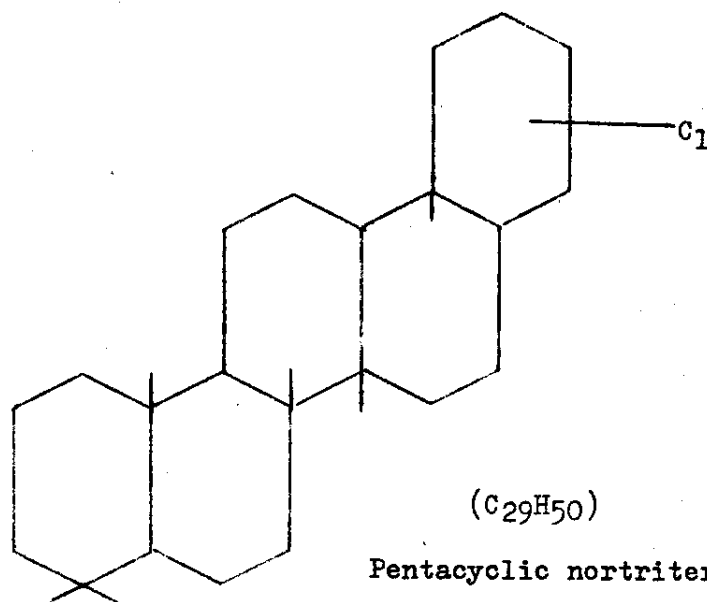
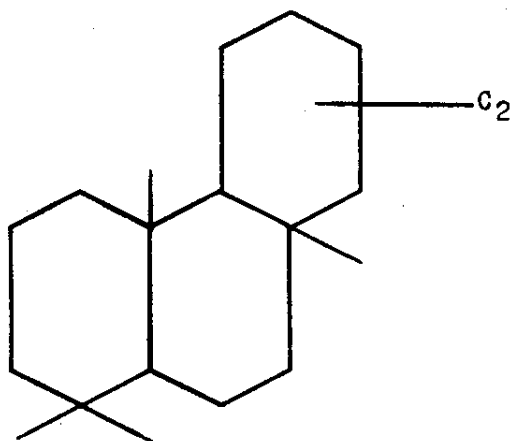
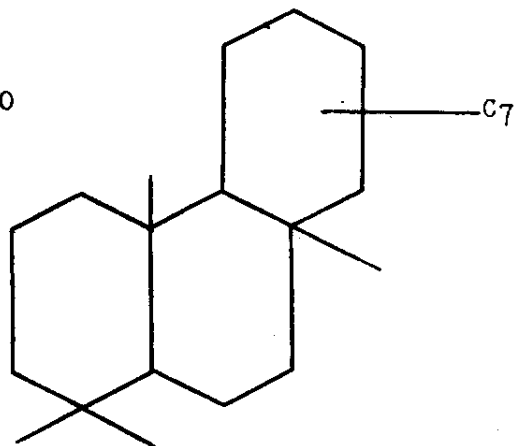


FIGURE 3A. continued

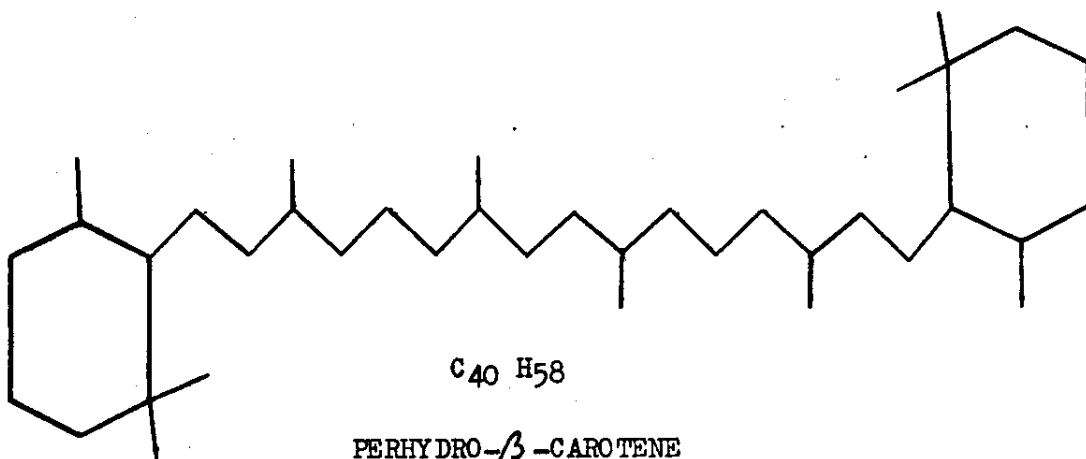


TO



$C_{20}H_{36}$  to  $C_{25}H_{46}$

TERPANES

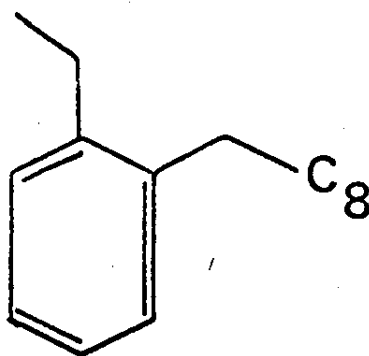


$C_{40}H_{58}$

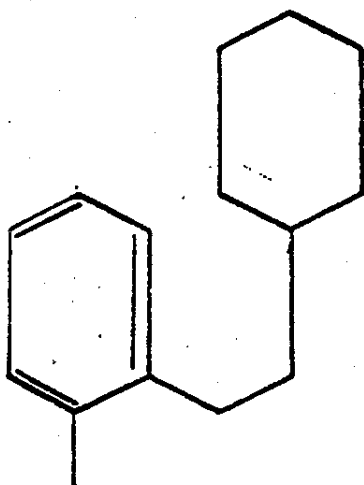
PERHYDRO- $\beta$ -CAROTENE

Figure 3A. continued

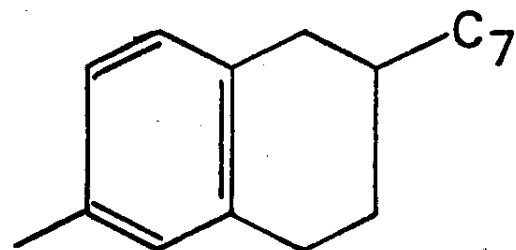
sixty) from the bitumen (soluble organic compounds) of Green River shale. He classified the aromatics into the five series;  $C_nH_{2n-6}$ ,  $C_nH_{2n-8}$ ,  $C_nH_{2n-10}$ ,  $C_nH_{2n-12}$ , and  $C_nH_{2n-14}$ . He also showed the most probable structure (Figure 3B) for them according to their IR, MS and GC spectrum. He used dehydrogenation technique to confirm the structures.



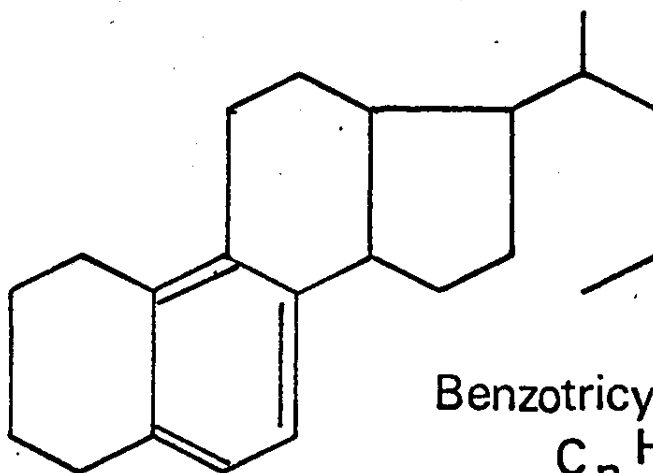
Alkylbenzene  
 $C_n H_{2n-6}$



Phenylalkane  
 $C_n H_{2n-8}$

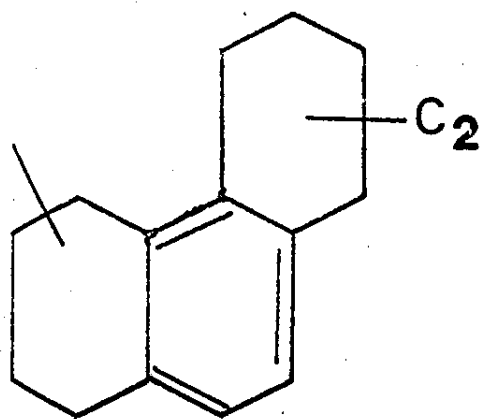


Benzomonocycloparaffin

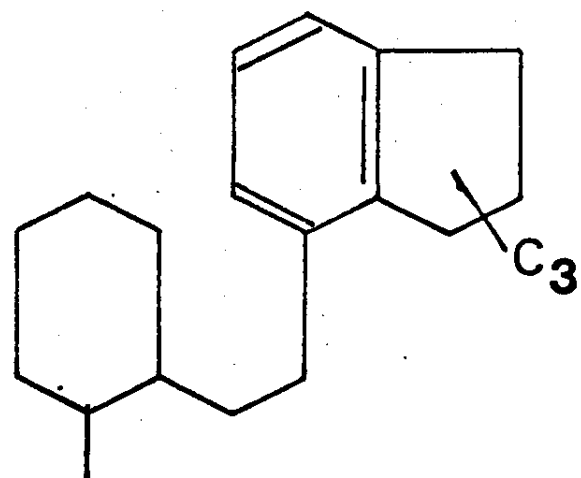


Benzotricycloparaffin  
 $C_n H_{2n-12}$

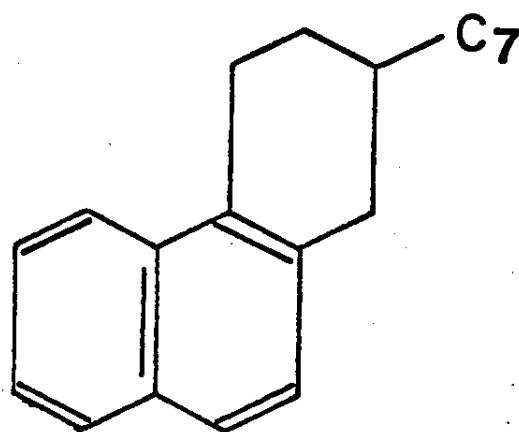
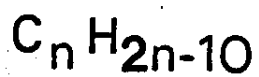
FIGURE 3B. Some structures of the saturated hydrocarbons in the bitumen of Green River Shale.



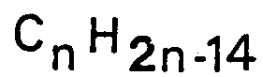
Benzodicycloparaffin



Indanalkane



Naphthalenecycloparaffin



## THE ORIGIN OF THE GREEN RIVER FORMATION

There have been some reports about the biological and non-biological origin of organic compounds extracted from Green River shales.

Ponnamperuma (1966 and 1968), Rudakov (1967), Calvin (1969) suggested the non-biological origin for fossil fuels and possible transition between non-living and living molecules. But, there is no strong evidence for accepting this supposition. The relationship between the existence of liquid hydrocarbons in recent sediments and the biological origin of petroleum were explained by Smith (1956). Meinschein (1959) showed the structural relation between some organic compounds in the lipid fraction of living organisms and the hydrocarbons in sediments and petroleum.

One of the principal processes for alteration of sediments is Bacterial Degradation which was described by Johnson and Calder in 1973.

The theory that algal oozes could give rise to oil shales is not a new one (Thiessen, 1925).

Han, et al (1968) analyzed the hydrocarbon constituents of four species of algae:

- 1) The blue-green algae (B.A.) like Nostoc and Anacystis.

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- 2) The green algae (G.A.) like spirogyra and chlorella. The results showed the presence of a series of normal hydrocarbons, n-C<sub>15</sub> to n-C<sub>20</sub>, with the n-C<sub>17</sub> hydrocarbon being the predominant member in each species. Some other interesting results were, existence of a monounsaturated C<sub>17</sub> hydrocarbon isolated from chlorella (G.A.), the branched alkanes, pristane and phytane which were isolated from the spirogyra (G.A.). The nostoc (B.A.) samples showed n-C<sub>17</sub> and 7,9-dimethylhexadecane as major hydrocarbons.

Bradley (1966) reported finding a lake (Mud Lake, Florida) that produces an organic ooze (Algae) which is considered to represent a modern analogue of the precursors of rich oil shales, such as the Green River shale. The sample from the lake was analyzed showing n-C<sub>20</sub> to n-C<sub>31</sub> alkanes. In 1967 Han, et al found carotenoids,  $\beta$ -carotene, and xanthophyll as the dominant pigment constituents of the Mud Lake extract.

Oro (1967) also showed a predominance of the n-C<sub>17</sub> in the Anacystis (B.A.). The rich oil shale from Green River Formation shows a bimodal pattern for normal hydrocarbons with a maximum at n-C<sub>17</sub> and n-C<sub>29</sub>. It also shows more odd-numbered hydrocarbons than even. The existence of an n-C<sub>17</sub> alkane in Green River oil shale can support the theory that algae, in part,

give rise to the organic material of rich oil shale.

Many organic compounds have been identified in the Green River shales: Carbohydrates by Palacas (1959), amino acids by Kvenvolden and Peterson (1969), porphyrins by Morandi and Jensen (1966), carboxylic acids by Abelson and Parker (1962), Lawlor and Robinson (1965), Leo and Parker (1966), Haug, et al (1967). These organic compounds match almost all of the major classes of building blocks in plant biochemistry. Furthermore, the organic matter of the Green River Formation is related to microscopic algae and other microorganisms. It is also derived from non-Lacustrine organic matter like pollen which was deposited in Uinta Lake in Utah and waxy spores which were deposited in Piceance Basin Lake in Colorado (Bradley 1970, Robinson, et al, 1965). In 1968 Han, et al, and in 1970 Bradley, suggested the cyanophyceae (the blue-green algae) which is a non-marine algae for the source material of Green River oil shale.

The biologic origin for the organic compounds extracted from crude oils and shales is more acceptable (Eglinton, et al (1964), Schroyer (1968), Hills, et al (1968)).

It seems there should be no doubt of the biological origin for the Green River Formation.

## EXPERIMENTAL

The samples studied in this investigation are:

Sample #1: Tar sand outcrop from Raven Ridge area in Utah. The sample has a dark tan color. It is dry and easy to pulverize.

Sample #2: Tar sand outcrop from the east side of White Rocks area in Utah. The sample has a dark brown color. It is sticky but easy to grain.

Sample #3: Tar sand outcrop from P. R. Spring area in Utah. The sample has a black color, and it is hard to grain.

Sample #4: Tar sand outcrop from the Sunny Side area in Utah. It is black and almost impossible to grain because of its hardness and stickiness.

Samples 1 to 4 were generously donated by Dr. A. Sherril Houghton.

Sample #5: Gilsonite, from the Cowboy-Bonanza system. It is black and easy to pulverize. The sample was donated by the American Gilsonite Company at Bonanza system (the same sample was used by Bonilla (1973)).

Sample #6: Oil shale from the Mahogany Marker tuff bed of the Green River Formation in Colorado. It was also donated by Dr. A. Sherrill Houghton.

Sample #7: Green River shale, donated by the U. S. Geological survey and identified as sample SGR-1, split 530 by the U.S.G.S.

Sample #8: Red Wash crude oil (lighter fraction) from well #15 in the Red Wash field in Utah.

Sample #9: Red Wash crude oil (heavier fraction) from Well #15 in the Red Wash field in Utah.

Samples 8 and 9 were donated to the chemistry department of the Colorado School of Mines by the University of Utah. The samples 6, 7, 8, and 9 are the same as Bonilla's samples.

#### Preparation of Reagents

Normal Hexane: Mallinckrodt, analytical reagent was distilled three times and washed with concentrated sulfuric acid in order to remove all the aromatic contaminants. It was then dried with  $\text{CaCl}_2$  and the presence of aromatic hydrocarbons checked by measuring the ultra violet absorption in the region of 200-300 NM (Beckman DK-2 spectrophotometer). Gas chromatographic analysis showed no contaminants.

Benzene: Mallinckrodt, analytical reagent, was distilled once without further purification.

Methyl Alcohol: Mallinckrodt, analytical reagent, was distilled once in a 40cm column packed with glass rings.

Carbon Tetrachloride: Mallinckrodt, spectrophotometric grade solvent, spectr AR<sup>tm</sup>. It was used as received.

Silica Gel: Baker analyzed reagent, 60-200 mesh size code 3405, suitable for chromatographic use, treated as described in this thesis.

#### The New Method of Pretreatment of Silica Gel

Silica gel was kept in 10% aqueous silver nitrate solution for ten minutes. It was filtered and rinsed with deionized water several times. Then, it was activated in a muffle at about 450° C for 48 hours, and kept under vacuum in a desiccator in the dark. This method has been reported in 1973 by Douglas and Grantham.

#### Extraction of the Bitumens

The soluble organic compounds (bitumen) from each sample were extracted with normal hexane. About 10 g. of each sample was taken and placed in a Soxhlet extractor, and extracted with 175 ml. normal hexane for 72 hours in order to extract the maximum amount of organic compounds. The solution was concentrated by passing a stream of air over the sample at room temperature.

A roto-evaporator was not employed in order to avoid loss

of the more volatile components (gas chromatographic analysis did show such loss of volatile hydrocarbons in the earlier analysis as a result of using a roto-evaporator).

During the passage of the stream of air, the sample was covered by a funnel to avoid contamination by dust. The concentrated solution was transferred into a weighed 10ml cap vial and dried further with nitrogen gas until the difference between two weighings was less than 0.5 mg. The yields of the bitumens so obtained are shown in Table II.

#### Liquid-Adsorption Chromatography

A glass 15mm ID column with Teflon valve was used with adsorbent/sample ratio of 1/100 for all tar sand samples.

About .5 g. of the bitumen from each sample was dissolved in n-hexane in 100ml volumetric flask. Twenty-five millilitres of that was taken and placed on top of the column which was packed with 60-200 mesh silica gel (pretreated with silver nitrate)..

Aliphatic Fraction: Normal hexane was used as the eluting solvent for the first cut, i.e., saturated hydrocarbons. The saturated hydrocarbons were collected in six to ten 50ml Erlenmeyer flasks and checked one by one for adsorption in

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SAMPLE	YIELD, wt%
Raven Ridge, Tar Sand out crop	3.86
East Side of White Rocks, Tar Sand out crop	5.30
P.R. Spring, Tar Sand out crop	9.62
Sunny Side, Tar Sand out crop	10.12
<b>Gilsonite</b> American Gilsonite Co. Cowboy Bonanza UTAH	<b>41.88</b>
Mahogany Marker Oil Shale	5.07
Green River Shale SGR-1, USGS	2.45

Table II: Yield of Bitumen Obtained by  
Extraction with Normal Hexane .

the ultra violet region, 220-300 NM (DK-2 Beckman spectrophotometer). No absorption was observed for any fraction proving the absence of aromatic hydrocarbons. These fractions were concentrated and dried as before.

Aromatic Fraction: Benzene was used as the eluting solvent for the second cut, i.e., aromatic hydrocarbons. This cut was concentrated and dried with nitrogen gas as before.

Asphaltene Fraction: Benzene/methanol (50-50%) was employed as the eluting solvent for the third cut, i.e., compounds more polar than the aromatics. The solution was concentrated with a Rinco-roto-evaporator using a vacuum pump, and dried with nitrogen gas to constant weight. A varying amount of solvent was required for each sample in order to elute the maximum amount of the hydrocarbons in each cut (Table III). Probably some polar materials were left on the column. The yield of each fraction is shown in Table IV and Vi.

#### Gas-Liquid Chromatography

The gas chromatograph (Beckman GC-5) at the Chemistry Department of Colorado School of Mines was employed. The chromatograph was equipped with two matched six feet length and 1/8 inch ID columns, packed with 3% Se-30 on 100-120 mesh Chromosorb-W

SAMPLE	REQUIRED AMOUNT OF SOLVENT, ml		
	N-HEXANE	BENZENE	BENZENE + METHANOL (50_50)%
GILSONITE , American Gilsonite Co.	150	150	150
RAVEN RIDGE , TAR SAND OUTCROP	250	250	250
EAST SIDE OF WHITE ROCKS, TAR SAND OUT- CROP	150	150	200
P.R.SPRING , TAR SAND OUTCROP	150	200	200
SUNNY SIDE , TAR SAND OUTCROP	200	200	250
*MAHOGANY MARKER OIL SHALE	125	125	125
* GREEN RIVER SHALE, SGR-1, U.S.G.S.	125	125	125
* RED WASH CRUDE OIL ( Lighter fraction)	125	125	125
* RED WASH CRUDE OIL (Heavier fraction)	125	125	125

TABLE III : The required amount of solvent for each cut.

\*The data were taken from Bonilla (1973).

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SAMPLE	total wt% paraffins	total wt% aromatics	total wt% asphaltene	remained in the column wt%
Raven Ridge, Tar Sand out crop	19.12	18.88	59.05	2.95
East Side of White Rocks, Tar Sand out crop	28.54	25.00	45.49	0.97
P.R. Spring, Tar Sand out crop	26.29	26.51	42.62	4.58
Sunny Side, Tar Sand out crop	33.46	24.26	33.36	8.92
Gilsonite, American Co.	10.63	12.80	32.33	44.24

Table IV: The yield of the fractions, liquid adsorption chromatography on silica gel.

SAMPLE	total wt% paraffins	total wt% aromatics	total wt% asphaltenes	remained in the column wt %
Gilsonite	<b>8.90</b>	<b>39.20</b>	<b>51.90</b>	<b>0.00</b>
Mahogany Marker Oil Shale	<b>19.60</b>	<b>22.60</b>	<b>57.80</b>	<b>0.00</b>
Green River Shale SGR-1, USGS	<b>20.80</b>	<b>22.10</b>	<b>57.10</b>	<b>0.00</b>
Red Wash Crude Oil (lighter fraction)	<b>61.90</b>	<b>30.80</b>	<b>7.20</b>	<b>0.10</b>
Red Wash Crude Oil (heavier fraction)	<b>58.60</b>	<b>33.10</b>	<b>8.30</b>	<b>.00</b>

Table V: The yield of the fractions, liquid adsorption chromatography,  
on silica gel

This table was taken from Bonilla (1973)

(high performance-acid washed).

A flame ionization detector was used with helium gas at about 277<sup>CC</sup>/min flow rate at 80 psig. The air flow rate was about 298<sup>CC</sup>/min at 40 psig. The hydrogen flow rate was 100<sup>CC</sup>/min at 40 psig. The flow rate of all three gases were checked after each run.

The speed of the chart was 0.5 in/min having different attenuation depending on the concentration of the sample. Inlet control was set at 78 and line was on 55 for all the samples. The total saturated fraction of each sample was dissolved in normal hexane and analyzed starting at 80<sup>o</sup>C and ending at 300<sup>o</sup>C in 32 minutes.

Standard solutions of pristane, phytane, and squalane were used in order to identify these important biological markers among the samples. Other saturated hydrocarbons can be determined from other workers for identification of the saturated hydrocarbon in the Green River Formation (these references are in the introduction).

The aromatic fraction of each sample was dissolved in benzene and analyzed starting at 100<sup>o</sup>C and ending at 300<sup>o</sup>C in 32 minutes. Almost all the aromatic compounds in the Green River oil shale have already been identified using GS, MS, and N.M.R. techniques by Anders (1972).

The GC spectrum of each sample is in the appendix.

#### Infrared Spectrometry

Perkin-Elmer, 521, Grating Infrared Spectrophotometer, at the research center of the Colorado School of Mines was used. Slit program was on 10, gain 4, attenuator speed 11, scan time 16, suppression 4, scale expansion IX, and source current 0.7 using potassium bromide sealed cell of 0.099mm thickness.

Each aromatic fraction was dissolved in 1cc of carbon tetrachloride for analysis. The reason for using solvent was because of the very small amount of aromatic sample and also because they were viscous liquids. The spectrum of the solvent and all other IR spectra are in the appendix.

Table VI shows the ratio of the aromatic CH. and saturated CH. in the aromatic fractions of the various tar sands and gilsonite.

SAMPLE	A <sup>⊕</sup>	B <sup>⊗</sup>
Raven Ridge	1.14 , 1.21	1.12
P.R. Spring	1.11 , 1.20	1.13
White Rocks	1.10 , 1.18	1.15
Sunny Side	1.08 , 1.17	1.19
Gilsonite	1.14 , 1.21	1.07

Table VI: The ratio of the unsaturated to saturated CH in the aromatic fraction.

$$\oplus \quad \frac{\text{Absorbance of C-H stretch of } =\text{C-H, at CH } 2930, 2910 \text{ cm}^{-1}}{\text{Absorbance of C-H stretch of } -\text{CH, at CH } 2823 \text{ cm}^{-1}}$$

$$\oplus \quad \frac{\text{Absorbance of C=C stretch, at } 1450 \text{ cm}^{-1}}{\text{Absorbance of C-H bending of alkyl groups, at CH } 1370 \text{ cm}^{-1}}$$

## DISCUSSION

The purpose of the work reported in this thesis is the study of the aliphatics and, mainly, aromatics of carbonaceous deposits of the Green River Formation and the investigation of improved methods of separation of aromatics from aliphatics, and also an understanding of the structures of compounds related to the biological markers of the Green River Formation in both fractions.

Advantages and Disadvantages of the New Method of Pretreatment of Silica Gel

There has always been a problem with elution of hydrocarbons contained in oil shale or petroleum: The amount of solvent is critical for each cut to prevent interference of one fraction with another especially the interference of aliphatics with aromatics.

This worker decided to pretreat silica gel to increase its ability to complex the aromatic hydrocarbons and slow their elution. Silver nitrate was selected for this purpose because silver/aromatic complexes are well known. The complex is probably a silver ion/aromatic complex.

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The advantages of this method are:

- 1) Because of a possible silver/aromatic complex or because of surface adsorption, the aromatic compounds do not elute with the aliphatic fraction, no matter how much hexane solvent is used. Without this method, control of the amount of solvent is necessary to elute only the aliphatics of the sample without interference by aromatics.
- 2) There is no need for a long column or a large amount of silica gel, therefore the absorbent sample ratio need not be as large. Previously, long columns were required to avoid interference of the aromatics in the aliphatic fraction, nevertheless, there was some loss of the aliphatics because of the long column, i.e., some high molecular aliphatics were left on the column.
- 3) Possibly because of the structure of the silver complex, the more polar aromatics can not be eluted easily, therefore, the second cut, i.e., the aromatic fraction can be obtained with good purity\*. Gilsonite showed 39.2% of aromatics with a previous method\*\* and 12.8% with the new method.

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\*The chromatogram shows better separation and sharper peaks.

\*\*Silica gel was pretreated with concentrated nitric acid, and a long column was used for liquid adsorption chromatography (Bonilla, 1973).

There might be just one disadvantage and this is the yield of the asphaltenes fraction which is decreased, i.e., the more polar compounds are more strongly retained on the column. This may not necessarily be a disadvantage since previous procedures may have mixed the polar compounds with the aromatics; gilsonite showed 32.33% asphaltenes in comparison with previous method which was 51.9%.

More research should be done to investigate the elution characteristics for this new method, i.e., the behavior of:

- 1) Polynuclear hydrocarbons such as alkylnaphthalenes, anthracenes, etc.
- 2) Ethers, both aromatic and aliphatic.

Gilsonite was selected for comparison of the two methods of pretreatment of silica gel to establish the advantages of the new procedure. In the new method gilsonite showed more total paraffins (10.6%) as compared to previous method (8.9%), and uncontaminated with aromatics.

The aromatic fraction of gilsonite obtained from the previous method (Figure 12-A) showed the presence of saturated hydrocarbons pristane and phytane. It also showed some compounds more polar than benzenoid aromatics eluting as evidenced by their elution in gas chromatography after the carotenoids.

The aromatic fraction of gilsonite obtained from the

method developed in this thesis (Figure 12) showed no saturated hydrocarbons. According to the chromatograms (Figure 12, Figure 12-A), there are lesser asphaltenes mixed with aromatics in the recent method than in previous method (the compounds which elute after the carotenoids).

#### Bitumens Analysis

P. R. Spring tar sand and Sunny Side tar sand have similar percentages (9.62, 10.12) of hexane soluble organic compounds (bitumen), and Raven Ridge tar sand has the lowest percentage (3.86) of bitumen among the tar sand samples (Table II).

White Rocks tar sand and Mahogany Marker oil shale have similar percentages (5.3, 5.07) of bitumen (Table II).

Gilsonite has the highest percentage (41.88) of the bitumen among the samples excepting Red Wash crude oil (100% soluble).

#### The Relationships of the Samples Drawn from L.A.C.\*

The bitumen extracted from White Rocks and P. R. Spring showed similar percentages of saturated hydrocarbons, aromatics, and asphaltenes (Table IV).

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\*Liquid adsorption chromatography

The Raven Ridge tar sand outcrop seems to be asphaltenic because the bitumen of the sample has lesser amounts of the saturated hydrocarbons and aromatics, and a larger amount of asphaltenes among the tar sand outcrop samples (Table IV). The Raven Ridge tar sand sample requires more solvent to completely elute the three cuts (fractions) apparently because it is more asphaltenic than the other samples (Table III).

Sunny Side tar sand is more paraffinic than the other samples. The percentage of the total paraffins is 33.46 (Table IV).

The Mahogany Marker oil shale and Green River shale (SGR-1, USGS) showed similar percentages of the total paraffins and almost the same percentages of the aromatics and more polar compounds (Table V, Bonilla, 1973).

The Red Wash crude oil (lighter and heavier fraction) is a very paraffinic crude (more than 60%). The sample has a very small amount of more polar compounds (Table V, Bonilla, 1973).

The data in Table V for the Red Wash crude oil is not precise, because some saturated hydrocarbons were eluted with the Red Wash crude oil aromatic fraction (data was taken from Bonilla, 1973).

Gilsonite showed a smaller amount of total paraffins than

the other samples.

The Relationships Among the Samples Drawn from G.L.C.\*

Total and Normal Saturated Hydrocarbons

All the tar sand samples, Raven Ridge, White Rocks, P. R. Spring, and Sunny Side have very similar paraffin distribution (Figures 3, 4, 5, and 6). Perhydro- $\beta$ -carotene was strongly indicated in the all tar sand samples. Pristane and phytane were identified for Raven Ridge and White Rocks tar sand outcrop, but in very small amounts (Figures 3 and 4). There is a strong possibility for the presence of pristane and phytane in P. R. Spring and Sunny Side tar sand outcrop (Figures 5 and 6).

Squalane was identified for Raven Ridge, P. R. Spring, and Sunny Side tar sand outcrop. There is also a good possibility for the presence of squalane in White Rocks tar sand in very small amounts.

In addition, all total paraffin chromatograms of the tar sand samples in this investigation were compared with total paraffin chromatogram of a tar sand sample from Asphalt Ridge, Vernal, Utah (Bonilla, 1973). The same total paraffins distribution was found as a result of that comparison. The

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\*Gas liquid chromatography

tar sand from Asphalt Ridge showed a typical paraffin distribution with  $n\text{-C}_{25}$  as the predominant hydrocarbon in the distribution. As a result of the extreme similarity between the total paraffins distribution of the tar sand samples in this investigation and the tar sand from Asphalt Ridge, it is quite possible that the  $n\text{-C}_{25}$  is the predominant normal paraffin in the Raven Ridge, White Rocks, P. R. Spring, and Sunny Side tar sand outcrop.

Pristane, phytane, and perhydro- $\beta$ -carotene are abundant in gilsonite. Gilsonite also has  $n\text{-C}_{25}$  as the predominant normal paraffin (ibid).

Mahogany Marker oil shale and Green River shale (SGR-1, USGS) have similar distribution of the normal paraffins with  $n\text{-C}_{31}$  and  $n\text{-C}_{29}$  as the predominant normal paraffin, respectively (ibid).

Red Wash crude oil (lighter and heavier fraction) is very paraffinic (more than 60%) with  $n\text{-C}_{25}$  as the predominant normal paraffin (ibid).

#### Aromatic Hydrocarbons

All the tar sand samples, Raven Ridge, White Rocks, P. R. Spring, and Sunny Side have very similar distribution of

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the aromatic hydrocarbons; especially White Rocks and P. R. Spring (Figures 8, 9, 10, and 11). Aromatic compounds are not abundant in Sunny Side tar sand outcrop (Figure 11). All the tar sand samples have carotenoids in common. Carotenoids have been found and identified in the oil shale of the Green River Formation (Anders, 1972).

Gilsonite, Green River Shale (SGR-1, USGS), and Mahogany Marker oil shale have very similar aromatic patterns; especially Mahogany Marker oil shale and Green River shale (SGR-1, USGS) have almost the same kind of aromatic distribution (Fig. 12,13,14).

The two Red Wash crude oil samples (lighter and heavier fraction) show no aromatic compounds above the background. They have very small amounts of aromatics which are not differentiable.

Two cycloalkanoaromatic hydrocarbons of the  $C_nH_{2n-12}$  series were indicated in gilsonite,  $C_{28}H_{44}$  and  $C_{29}H_{46}$ . These two hydrocarbons have been found and identified in the oil shale of the Green River Formation and confirmed with MS and IR techniques by Anders in 1972.

The "parent" molecular ions of these hydrocarbons are shown in Table VII. The data were taken from Anders, 1972.

These two hydrocarbons plus one other hydrocarbon ( $C_{27}H_{42}$ , which is possibly present in gilsonite) were isolated gas

chromatographically as a mixture (Anders, 1972). The ions of diagnostic value and the intensities of the mixture are shown in Table VIII.

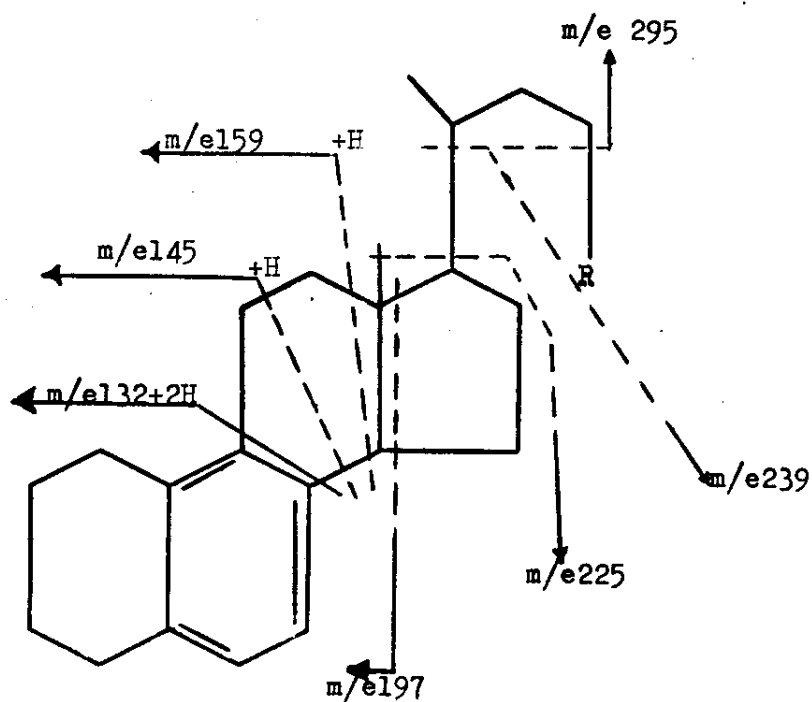
The data in Table VIII can help in suggesting a possible skeletal structure for the compounds ( $C_{27}H_{42}$ ,  $C_{28}H_{44}$ ,  $C_{29}H_{46}$ ).

The compounds with four rings, which are structurally related to steroids, are abundant in the Green River Formation, Burlingame, et al (1965), Henderson, et al (1968), Anderson, et al (1969), Anders and Robinson (1971), Gallegos (1971). The similar compounds having four rings (just one ring is aromatic) should be considered for the  $C_{27}H_{42}$ ,  $C_{28}H_{44}$ ,  $C_{29}H_{46}$ . According to the aromatic chromatogram of gilsonite (Figure 12), there is a very optimistic possibility of the existence of  $C_{27}H_{42}$  in gilsonite. Unfortunately, this worker was not able to identify  $C_{27}H_{42}$  because of lack of facilities. In further work,  $C_{27}H_{42}$  may be synthesized to establish its presence in gilsonite, and probably in tar sand of the Green River Formation.

The Structure I is considered to be the most probable structure for the  $C_nH_{2n-12}$  series.

Empirical formula	Empirical mass*	Observed mass*	Molecular ion
C <sub>28</sub> H <sub>44</sub>	380.3442	380.3453	380
C <sub>29</sub> H <sub>46</sub>	394.3598	394.3611	394

Table VII: Parent molecular ions in C<sub>28</sub> H<sub>44</sub> and C<sub>29</sub> H<sub>46</sub>.  
 \*Based on <sup>12</sup>C=12.0000



Structure I

Relative intensity	m/e	Relative intensity	m/e
62	91	18	239
62	105	14	253
100	119	6	267
49	128	6	281
40	133	6	295
49	145	14	351
49	157	3	365
34	159	14	379
28	173	14	366 (M)
34	197	11	380 (M)
17	211	8	394 (M)
14	225		

Table VIII : The mass spectral data of the mixture of  
C<sub>27</sub> H<sub>42</sub> , C<sub>28</sub> H<sub>44</sub> , and C<sub>29</sub> H<sub>46</sub> .

\*Data were taken from Anders 1972 .

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### Infrared Analysis Relations Among the Samples

The aromatic fractions of the tar sand samples and gilsonite have similar kinds of IR spectra, probably indicating that they contained compounds of very similar structure. This worker was hoping to get a correlation between the unsaturated rings and the saturated rings and chains of the aromatic compounds by studying the absorbance of C-H and c=c stretch and C-H bending. All of the tar sand samples and gilsonite have the same frequencies of C-H stretching, c=c stretching, C-H bending, which gives a strong indication of similar skeletal structures for them. Of course, further investigation (like isolation of some aromatics from the fractions) is required to confirm this supposition.

The attempt to find a significant variation between the ratio of the unsaturated C-H and saturated C-H in the aromatic fractions failed (Table VI).

## CONCLUSIONS

The following conclusions were drawn using the method developed in this thesis for pretreatment of silica gel in comparison with other methods:

- 1) No close control of solvent for elution purposes is required, permitting full recovery of saturated hydrocarbons.
- 2) There is no interference of aromatic in aliphatic fractions or vice versa.
- 3) There is a difference in the amount of the aromatic fraction compared with using untreated silica gel. What this change implies must be investigated further, but this worker believes that this method gives the opportunity to separate the aromatic hydrocarbons having one aromatic ring (mono nuclear) from aromatic hydrocarbons having two aromatic rings (dinuclear aromatic) which are more polar than mono-nuclear aromatic hydrocarbons.
- 4) This procedure is probably inadequate for complete recovery of the asphaltene fraction.

The following facts were drawn from L.A.C.\* and G.L.C.\* analysis:

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\*Liquid adsorption chromatography and gas liquid chromatography

There is a similar composition of the bitumens extracted from White Rocks and P. R. Spring tar sand outcrop.

The Raven Ridge tar sand is more asphaltenic than the other tar sand samples (White Rocks, P. R. Spring, and Sunny Side).

Sunny Side tar sand is more paraffinic than the other tar sand samples.

All the tar sand samples, Raven Ridge, White Rocks, P. R. Spring, and Sunny Side are extremely similar in the distribution of total paraffins all containing perhydro- $\beta$  carotene. They are also alike in the distribution of the aromatics, all containing carotenoids. The distribution of total paraffins of the tar sand samples matches the tar sand sample from Asphalt Ridge. Therefore, there is a good possibility for the tar sand samples of this investigation to have  $n\text{-C}_{25}$  as the predominant normal paraffin. If it is true, a common source for these tar sands is indicated.

Raven Ridge and White Rocks have only a small amount of pristane and phytane.

Raven Ridge, P. R. Spring, and Sunny Side contain squalane.

The aromatic distribution of White Rocks and P. R. Spring are extremely similar, they also have similar composition of the bitumens.

The aromatics are not abundant either in Sunny Side tar sand outcrop or in Red Wash crude oil, but aromatics are abundant in gilsonite, Green River shale (SGR-1, USGS), and Mahogany Marker oil shale. The patterns of aromatics are very similar in gilsonite, Green River shale (SGR-1), and Mahogany Marker oil shale.

The similarities of aromatics and aliphatics which have been found among the tar sand samples lead this worker to suggest that these four bituminous materials came originally from the same source.

The relationship which has been found among the aromatics of Raven Ridge tar sand, White Rocks tar sand, P. R. Spring tar sand, and gilsonite can suggest that they originated from crude oil in the Green River Formation which migrated from its original reservoir to where the samples were taken today.

The Red Wash crude oil is an especial kind of crude oil (so paraffinic) which migrated from the original reservoir (secondary migration) and possibly left the aromatics and more polar compounds behind.

APPENDIX  
CHROMATOGRAMS

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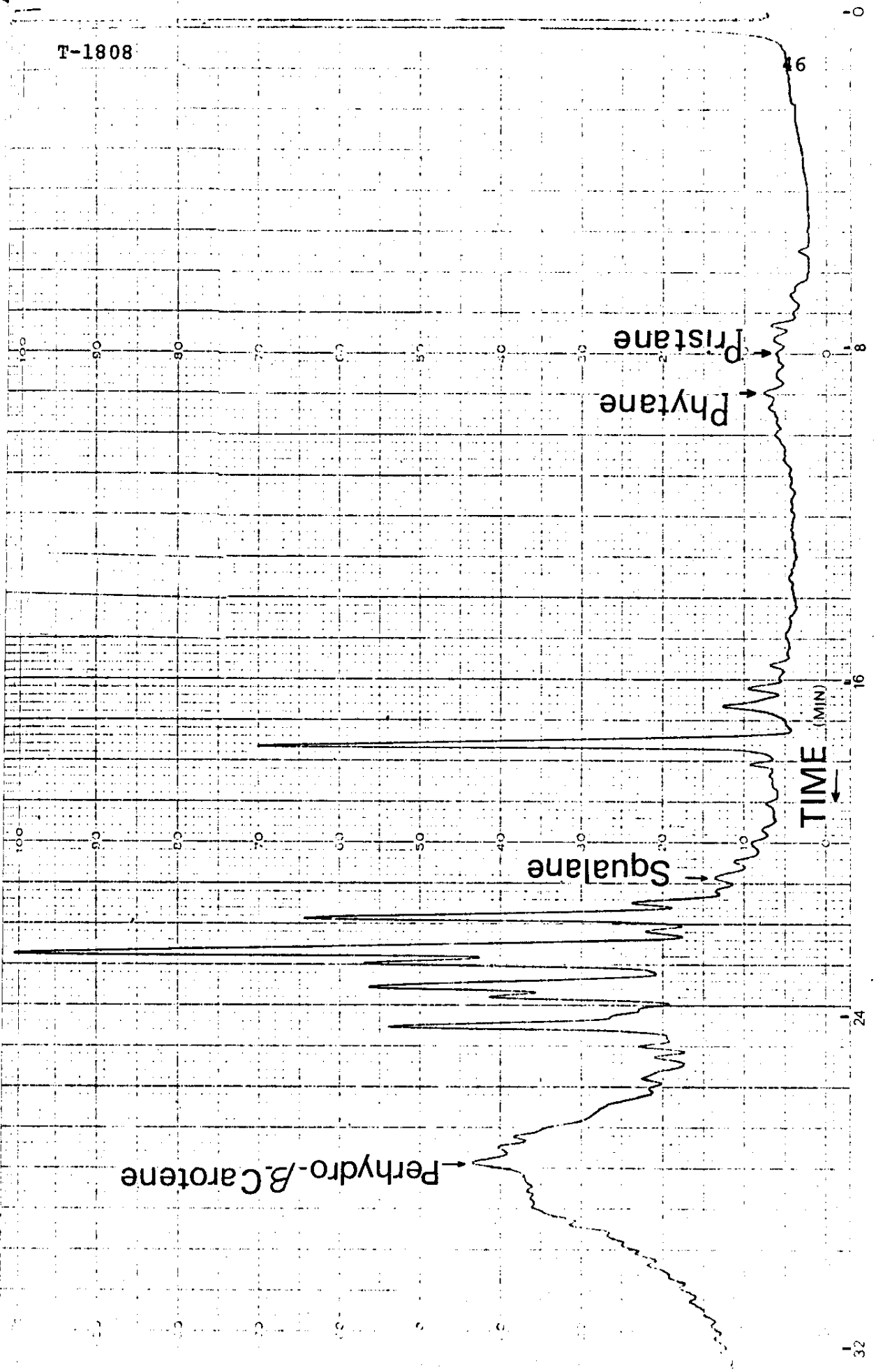


FIGURE 3. CHROMATOGRAM OF TOTAL SATURATED FRACTION OF RAVEN RIDGE TARSAND, OUTCROP.

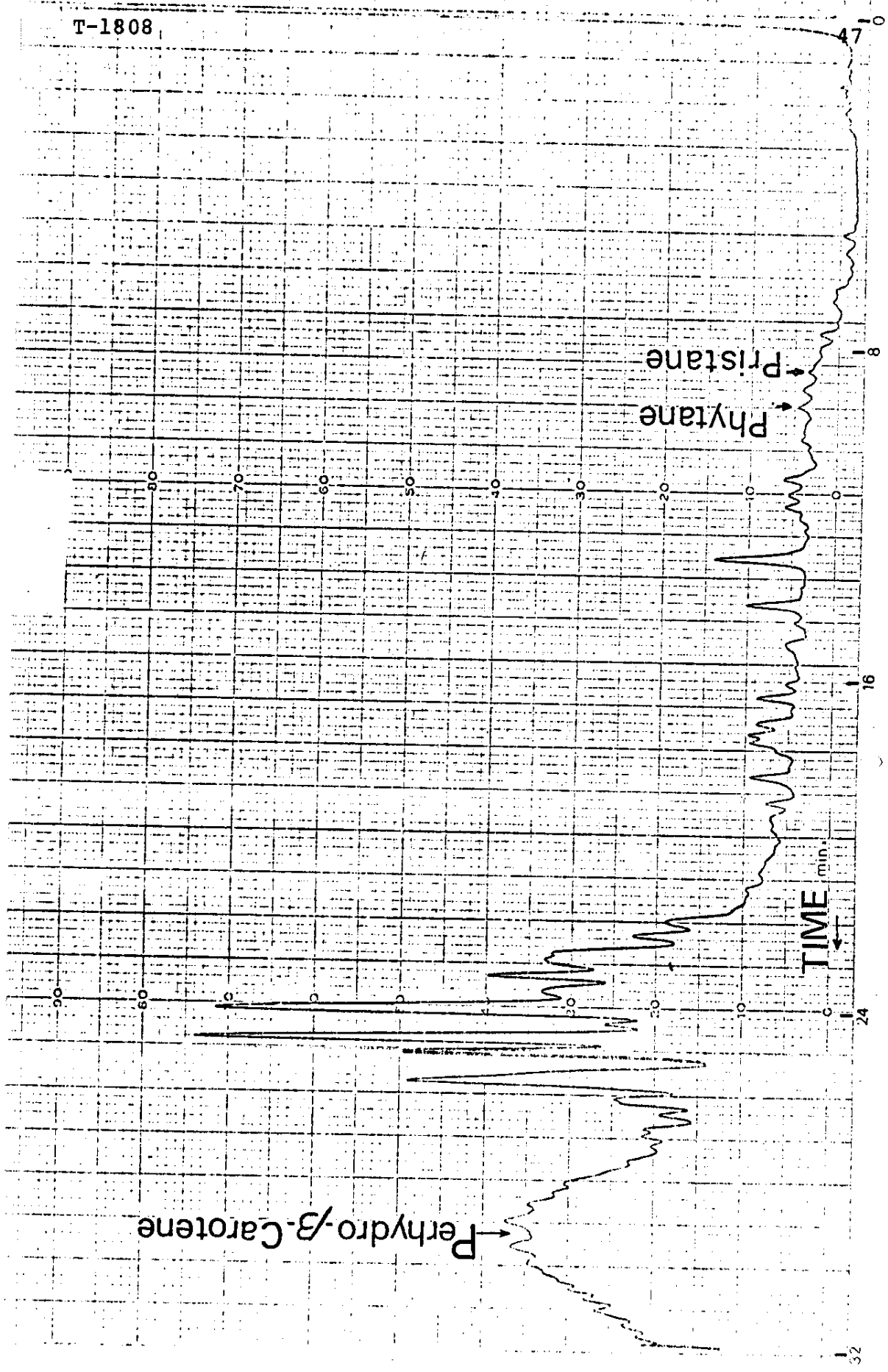


FIGURE 4. CHROMATOGRAM OF TOTAL SATURATED FRACTION OF WHITE ROCKS TARSAND OUTCROP.

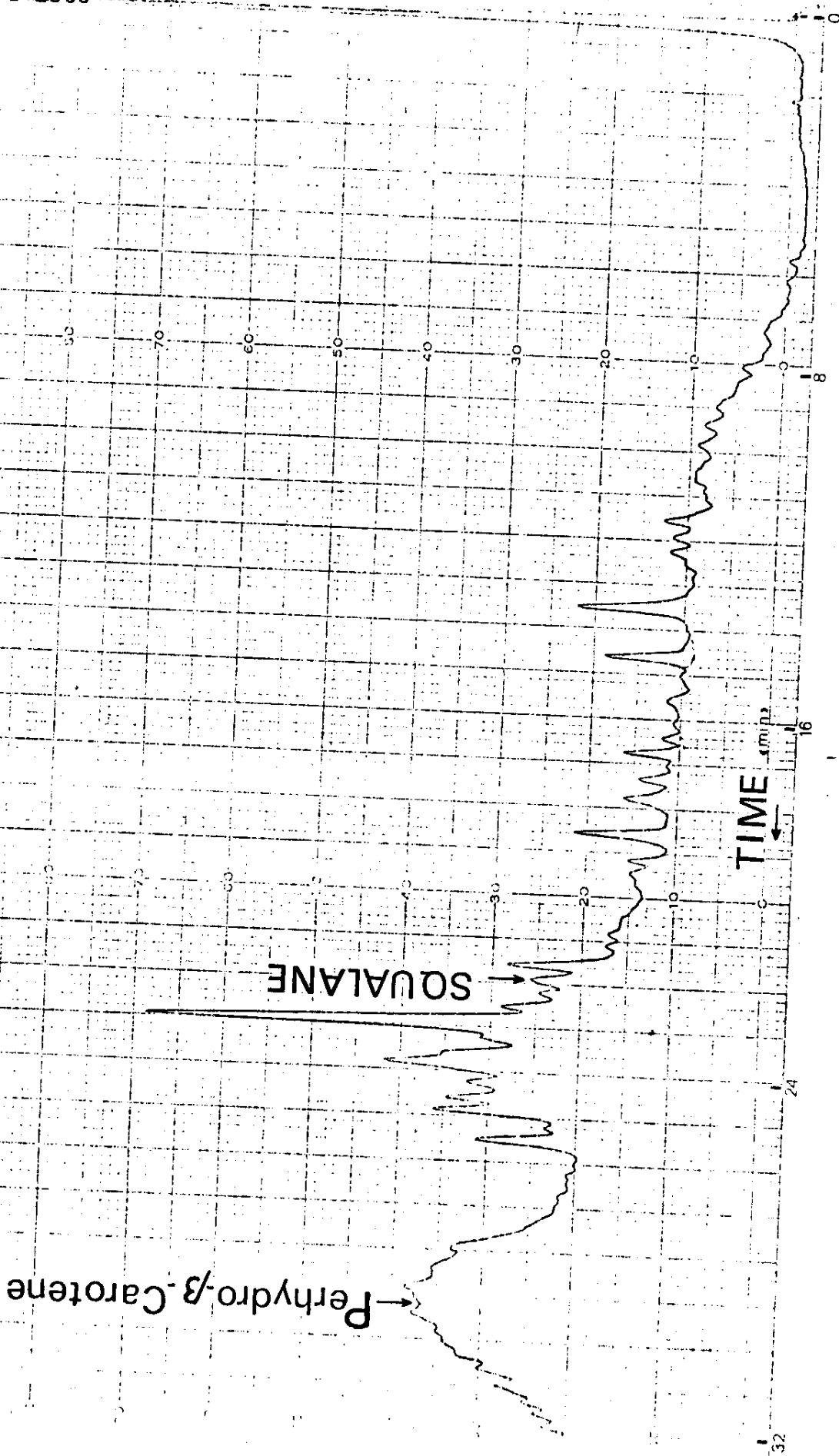


FIGURE 5. CHROMATOGRAM OF TOTAL SATURATED FRACTION OF P.R. SPRING TARSAND OUTCROP.

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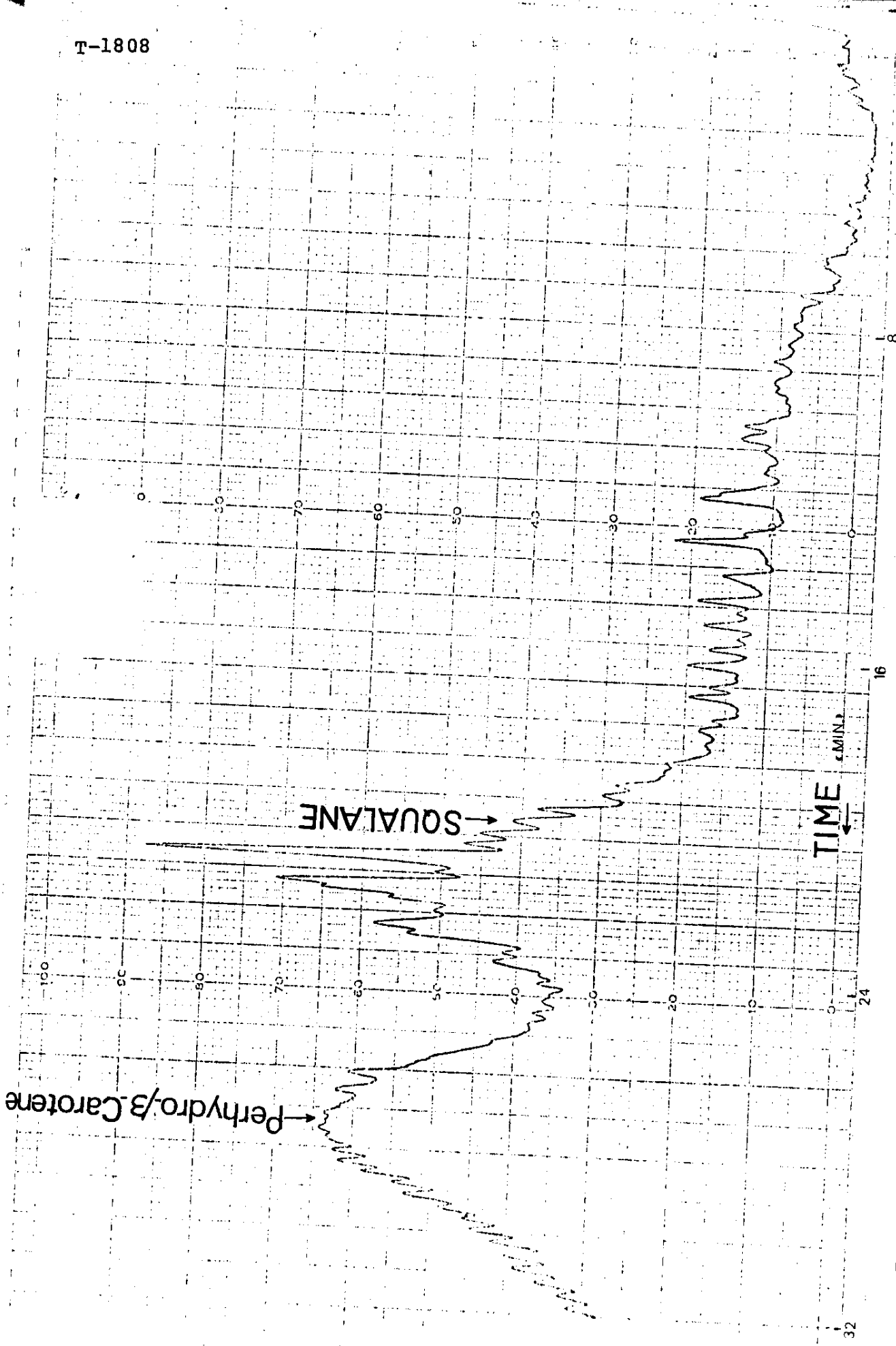


FIGURE 6. CHROMATOGRAM OF TOTAL SATURATED FRACTION OF SUNNY SIDE TARSAND OUTCROP.

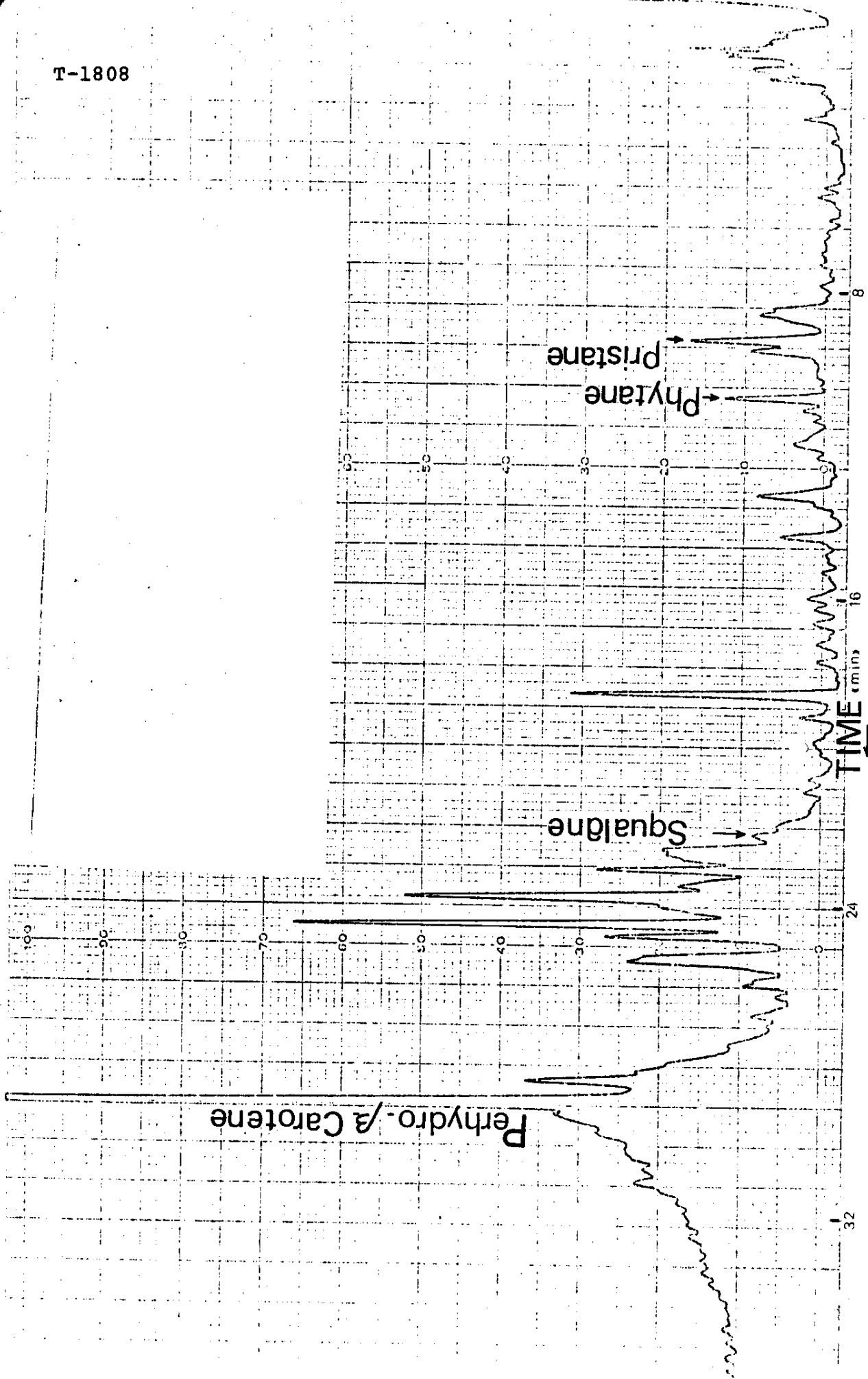


FIGURE 7. CHROMATOGRAM OF TOTAL SATURATED FRACTION OF GILSONITE.

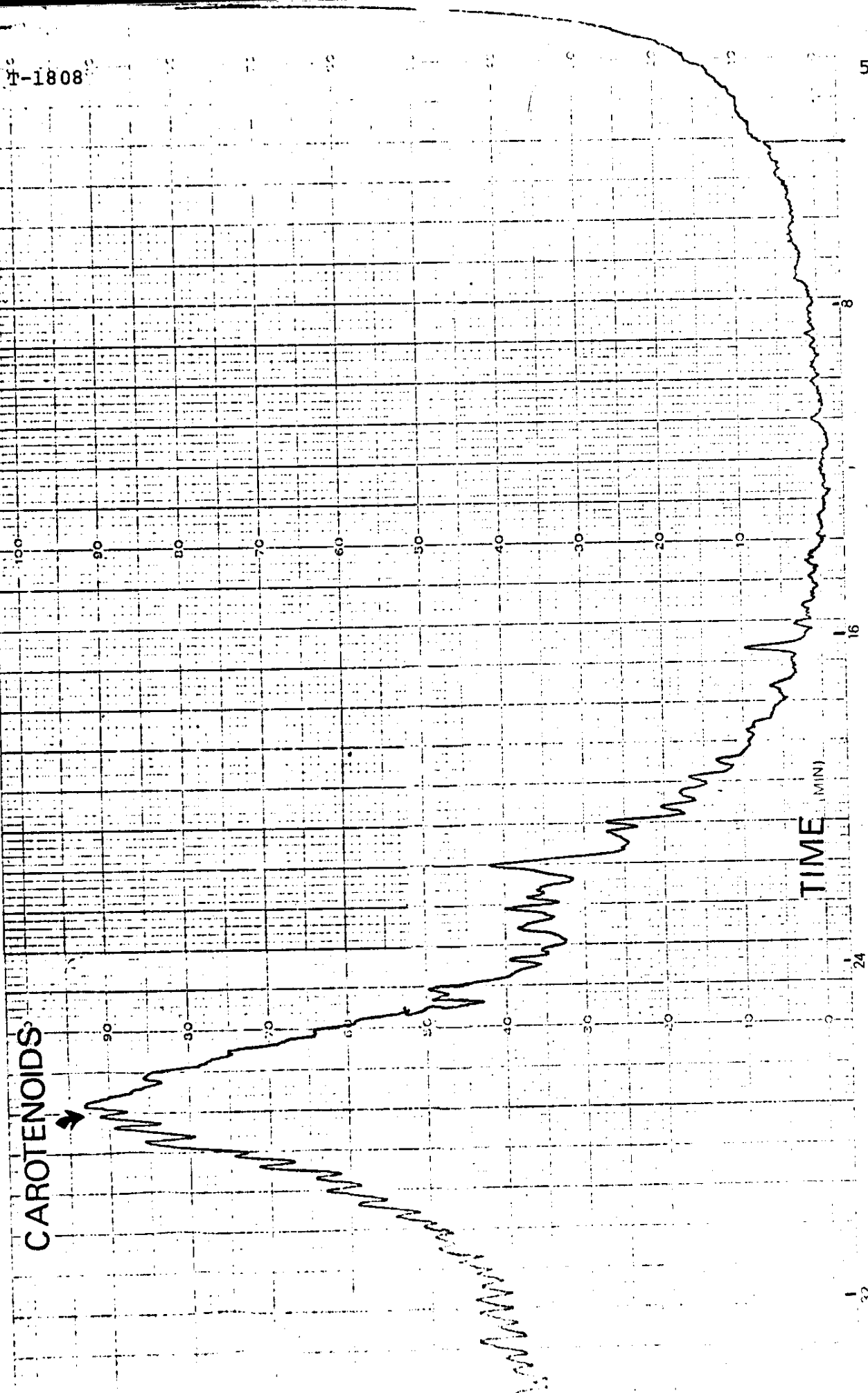


FIGURE 3. CHROMATOGRAM OF THE AROMATIC FRACTION OF RAVEN RIDGE TARSAND OUTCROP.

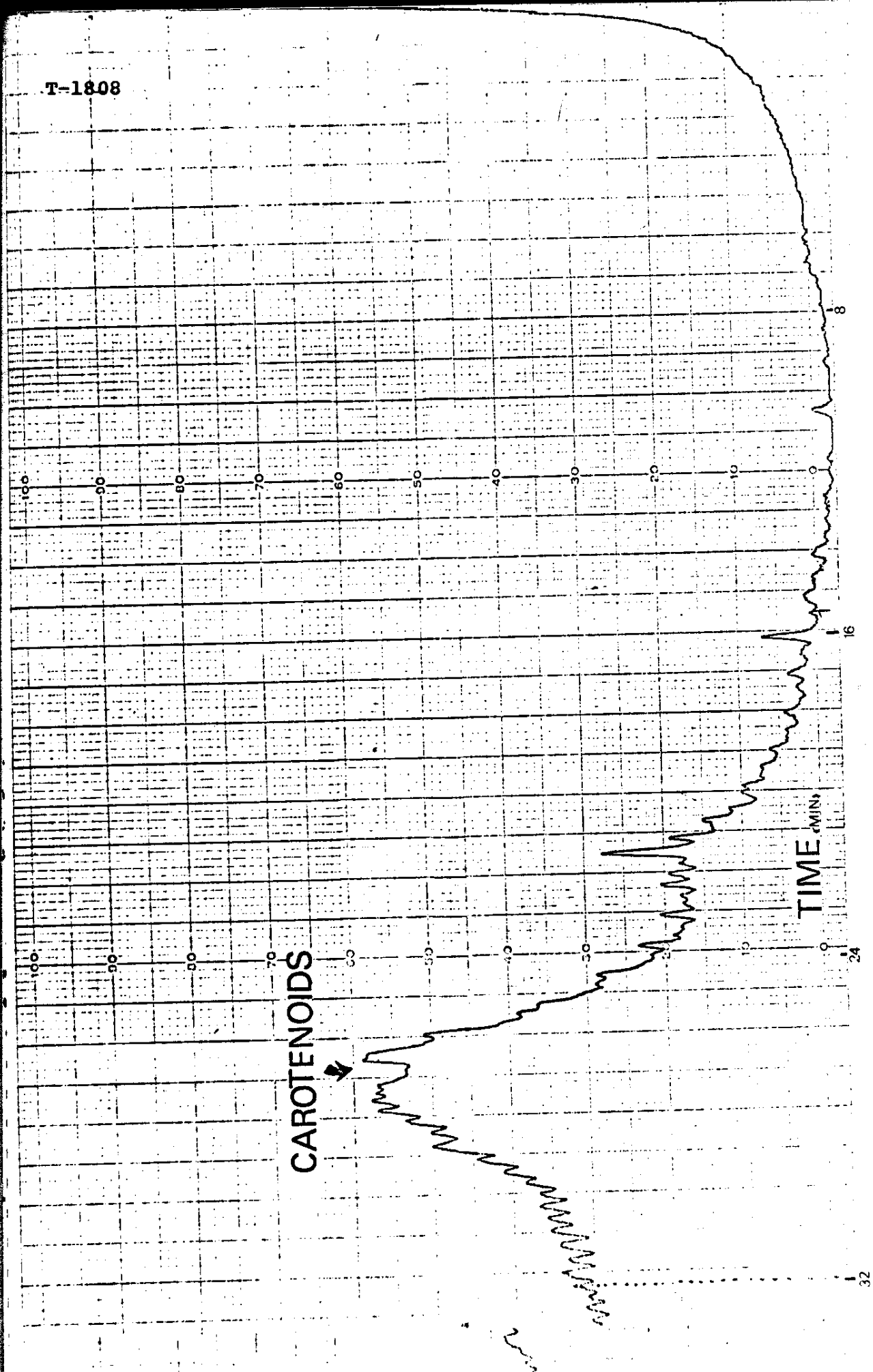


FIGURE 9. CHROMATOGRAM OF THE AROMATIC FRACTION OF WHITE ROCKS TARSAND OUTCROP.

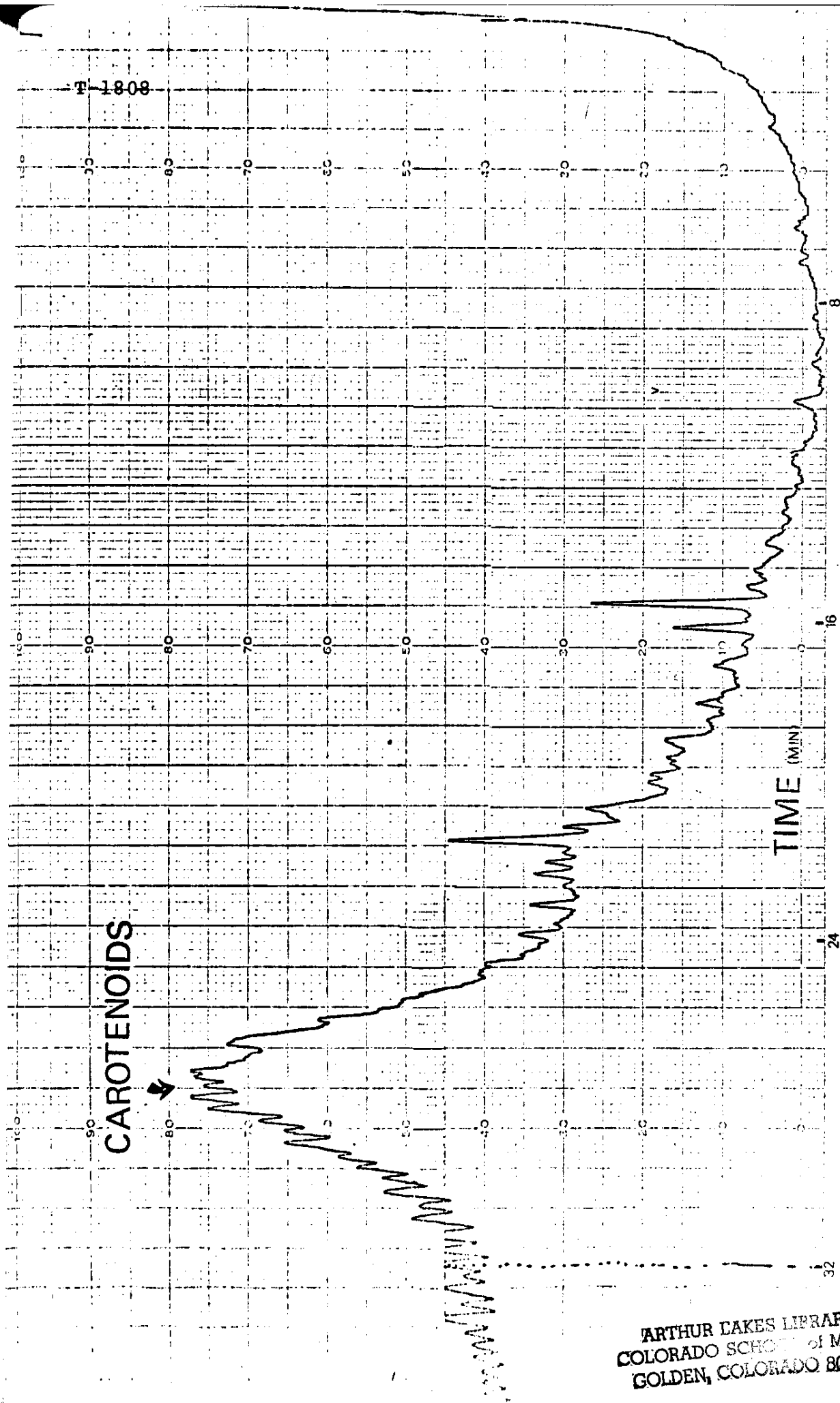


FIGURE 10. CHROMATOGRAM OF THE AROMATIC FRACTION OF P.R. SPRING TARSAND OUTCROP.

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CAROTENOIDS



TIME (MIN)

32

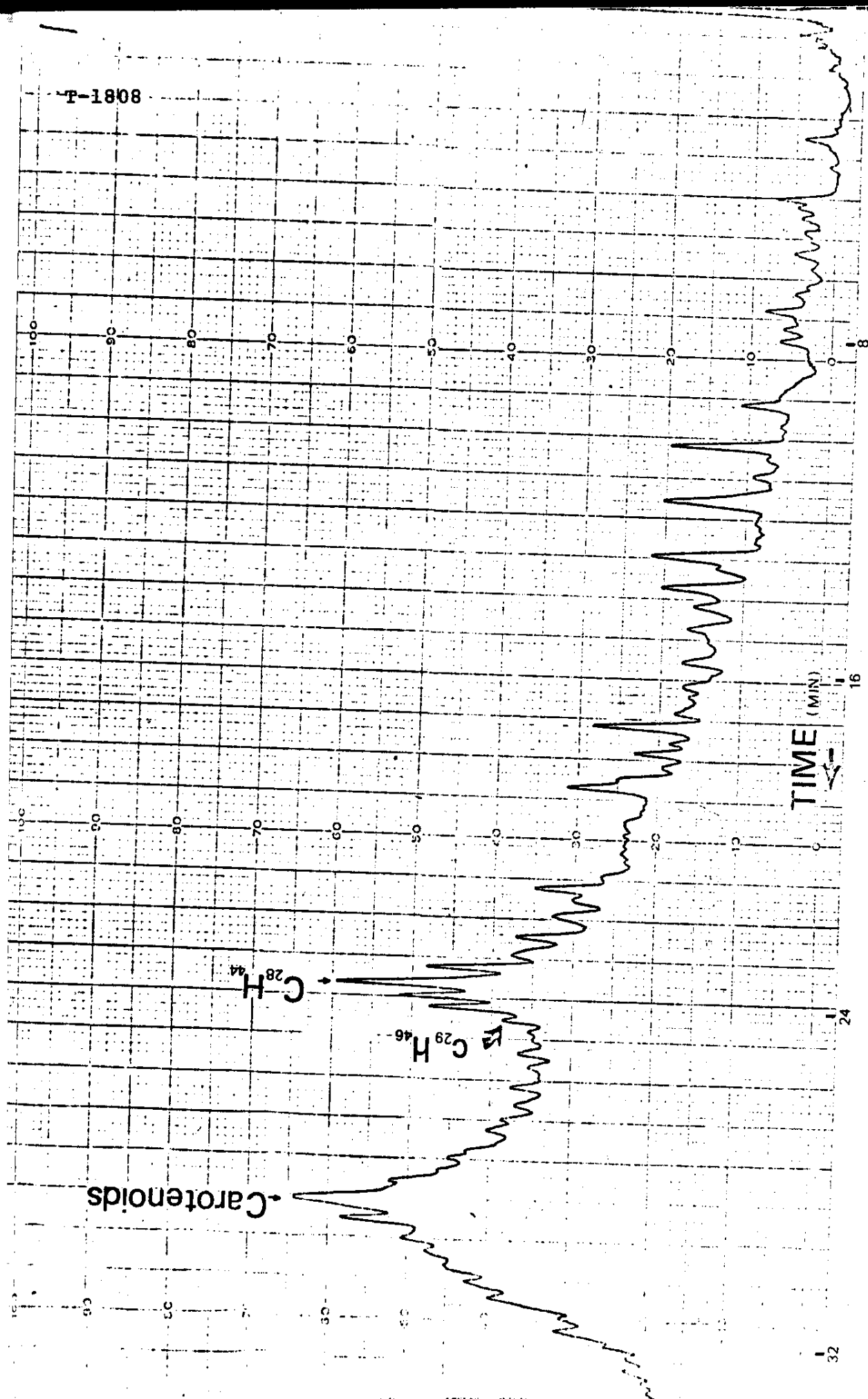
24

16

8

0

FIGURE 11. CHROMATOGRAM OF THE AROMATIC FRACTION OF SUNNY SIDE TARSAND OUTCROP.



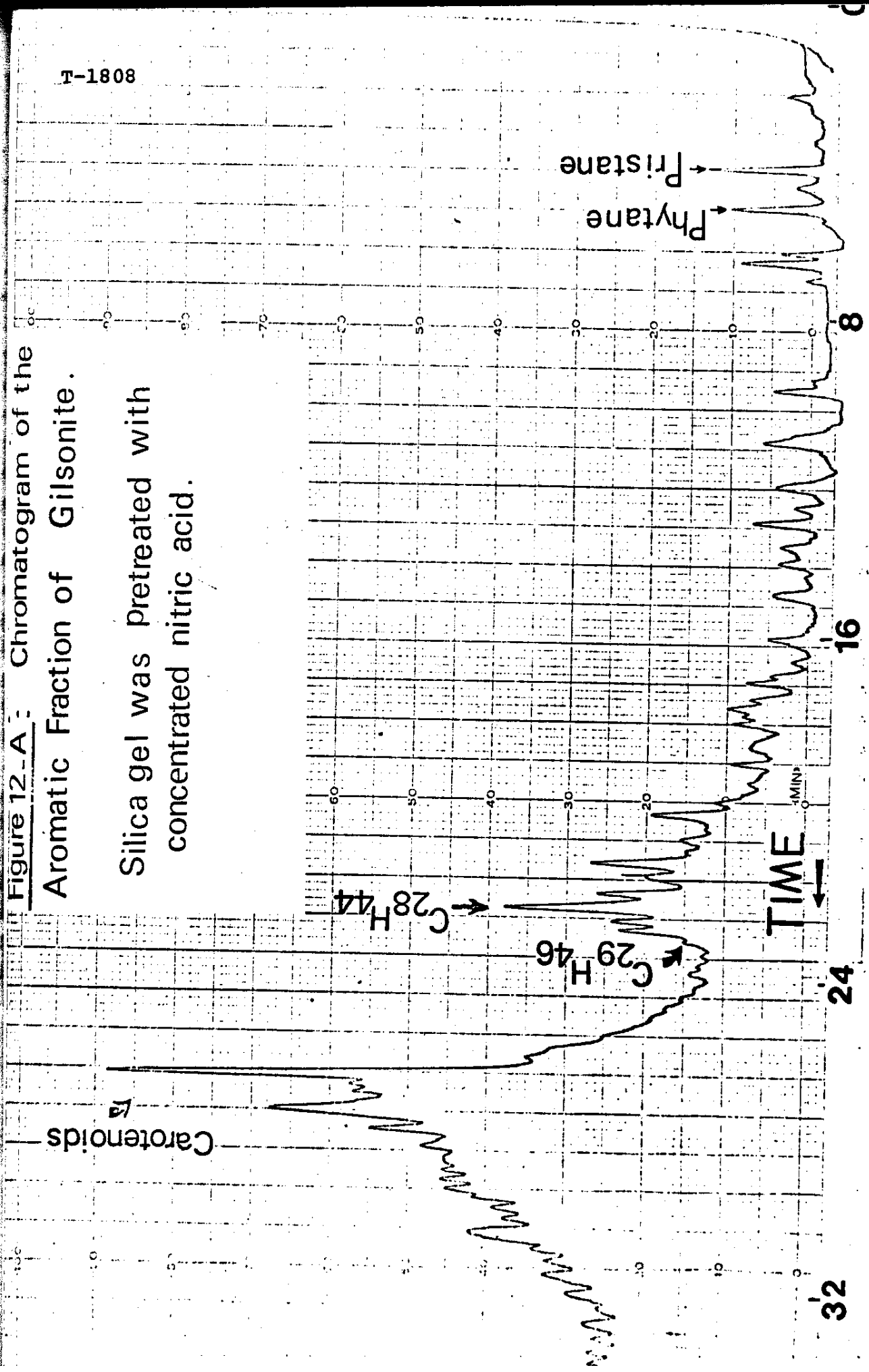
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FIGURE 12. CHROMATOGRAM OF THE AROMATIC FRACTION OF GILSONITE.

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Figure 12-A: Chromatogram of the Aromatic Fraction of Gilsonite.

Silica gel was pretreated with concentrated nitric acid.



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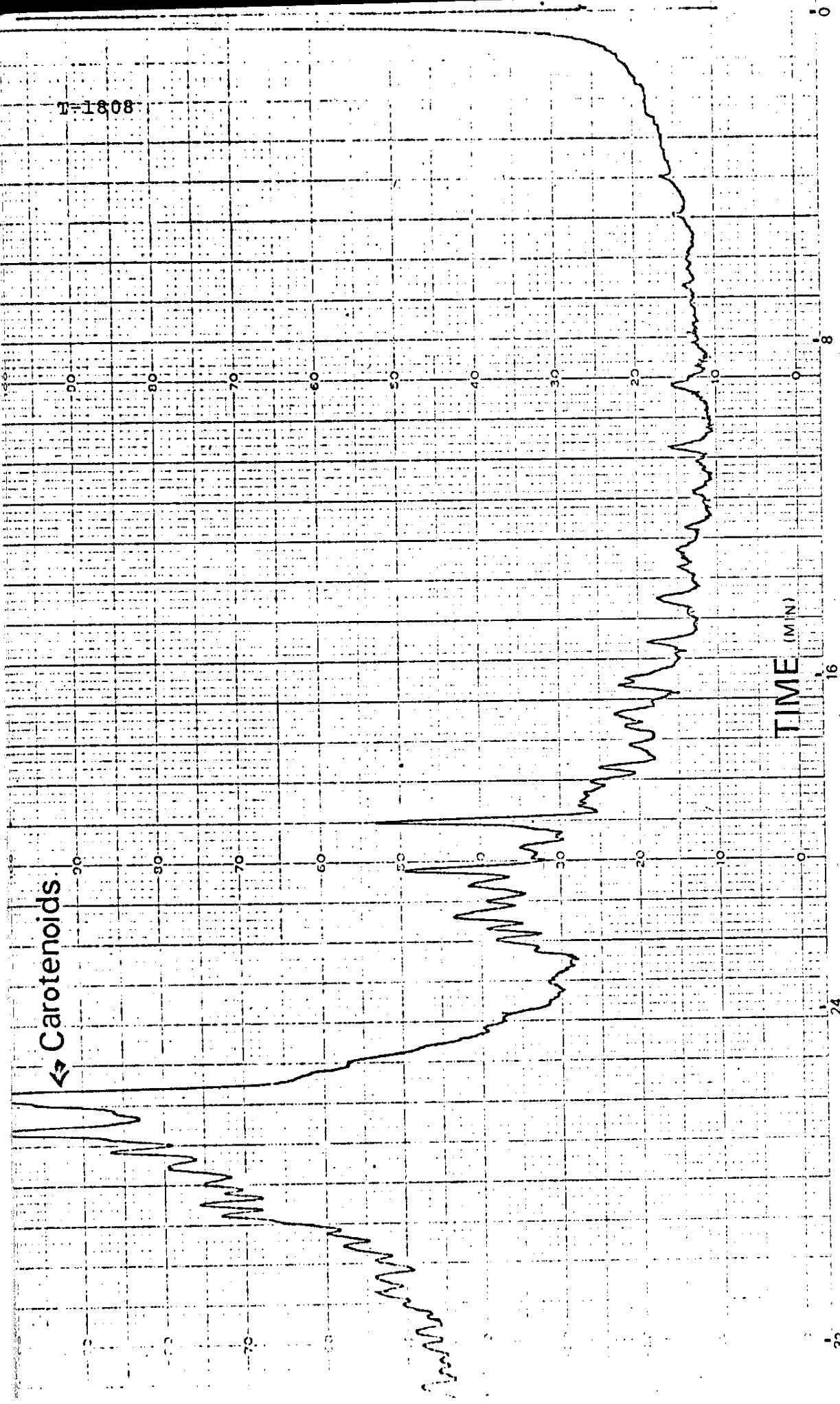


FIGURE 13. CHROMATOGRAM OF THE AROMATIC FRACTION OF MAHOGANY MARKER OIL SHALE.  
 (SILICA GEL WAS PRETREATED WITH CONCENTRATED NITRIC ACID.)

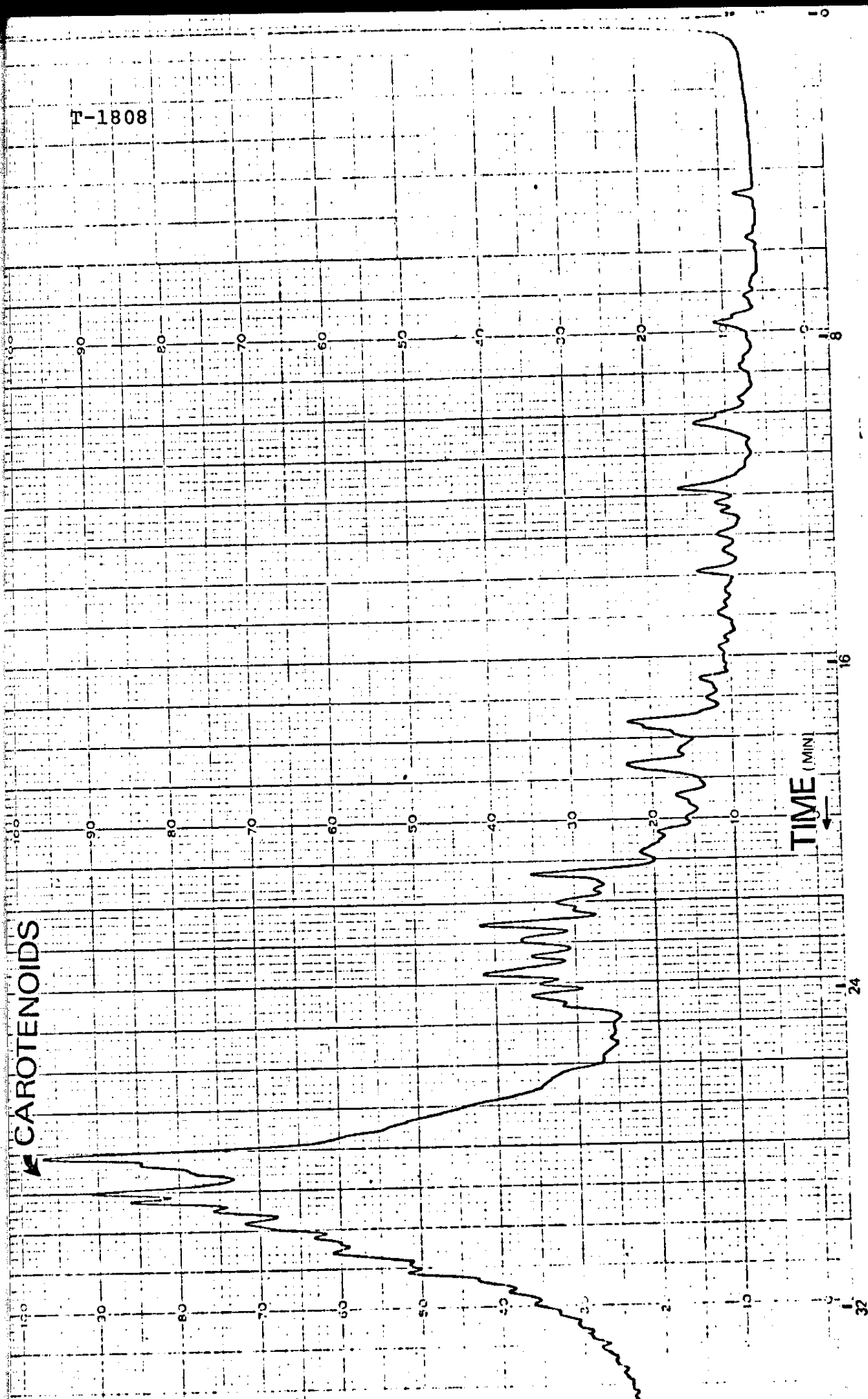
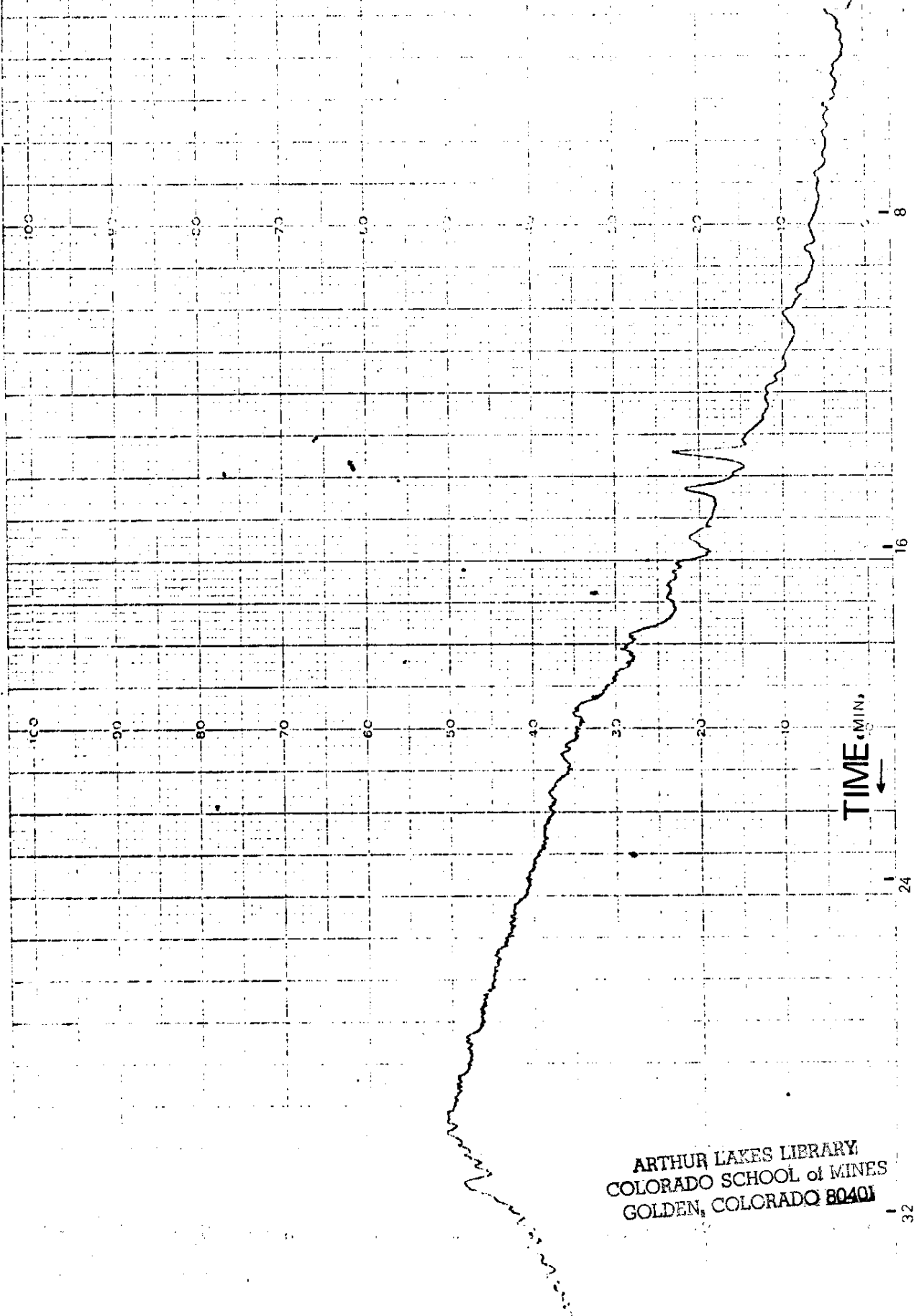


FIGURE 14. CHROMATOGRAM OF THE AROMATIC FRACTION OF GREEN RIVER SHALE, SGR-1, U.S.G.S.

(SILICA GEL WAS PRETREATED WITH CONCENTRATED NITRIC ACID.)

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59

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FIGURE 15. CHROMATOGRAM OF THE AROMATIC FRACTION OF RED WASH CRUDE OIL (LIGHTER FRACTION).

32

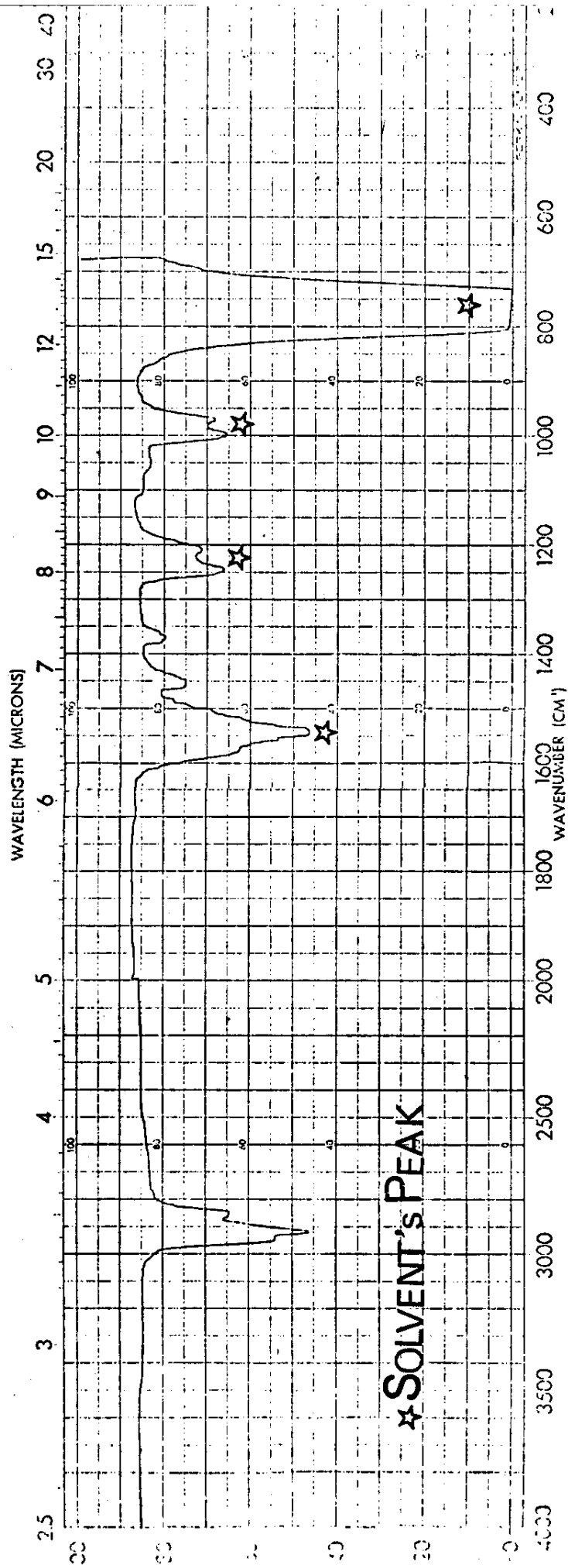


FIGURE 16. INFRARED OF THE AROMATIC FRACTION OF GILSONITE

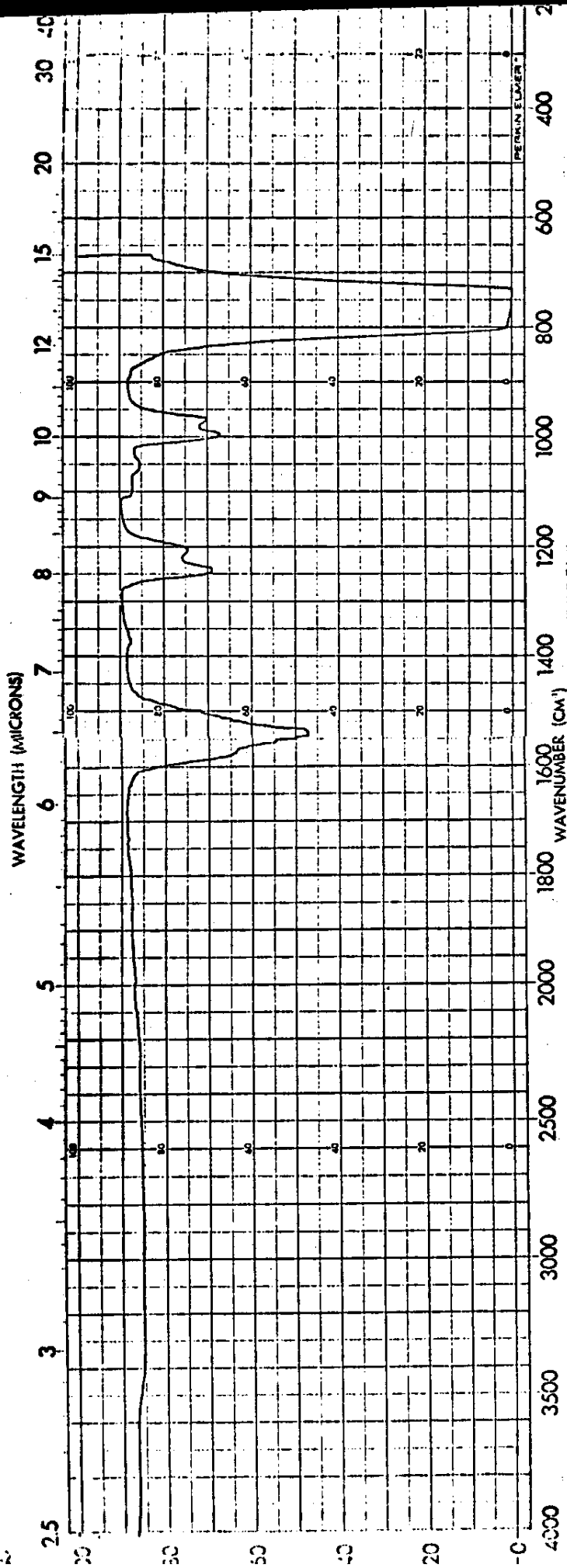


FIGURE 17. INFRARED SPECTRUM OF CARBON TETRACHLORIDE.

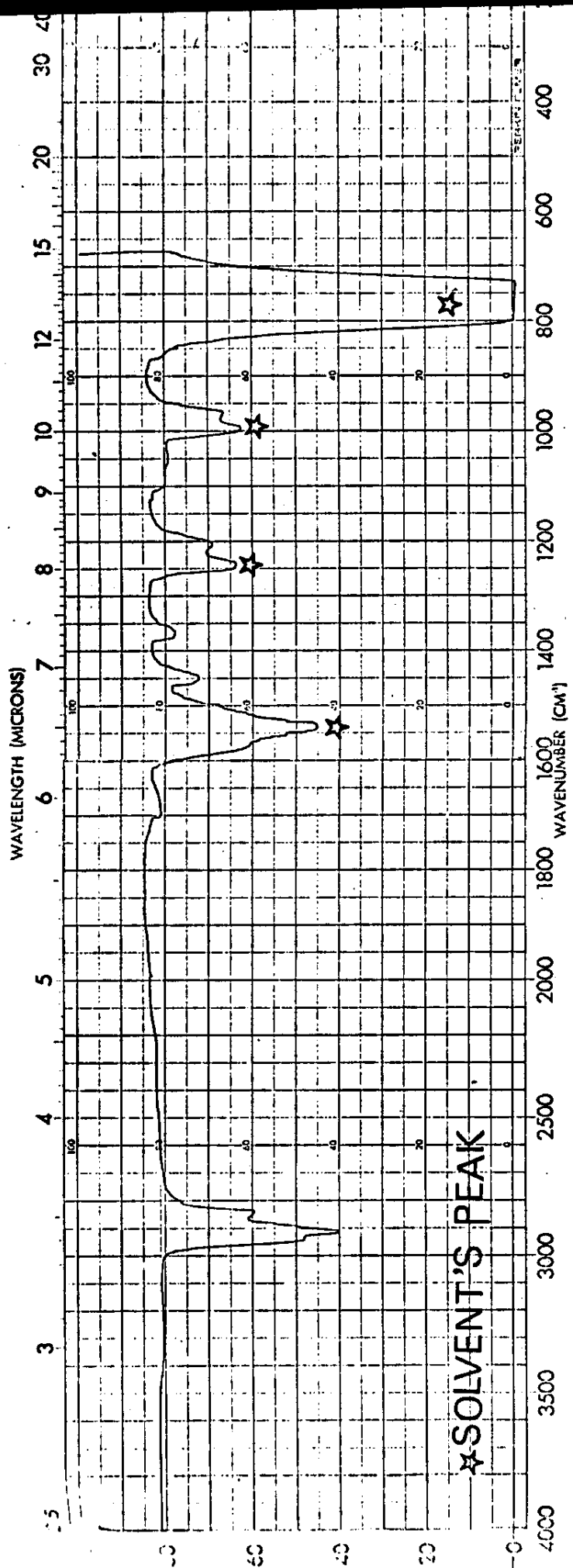


FIGURE 18. INFRARED SPECTRUM OF THE AROMATIC FRACTION OF RAVEN RIDGE TARSAND OUTCROP.

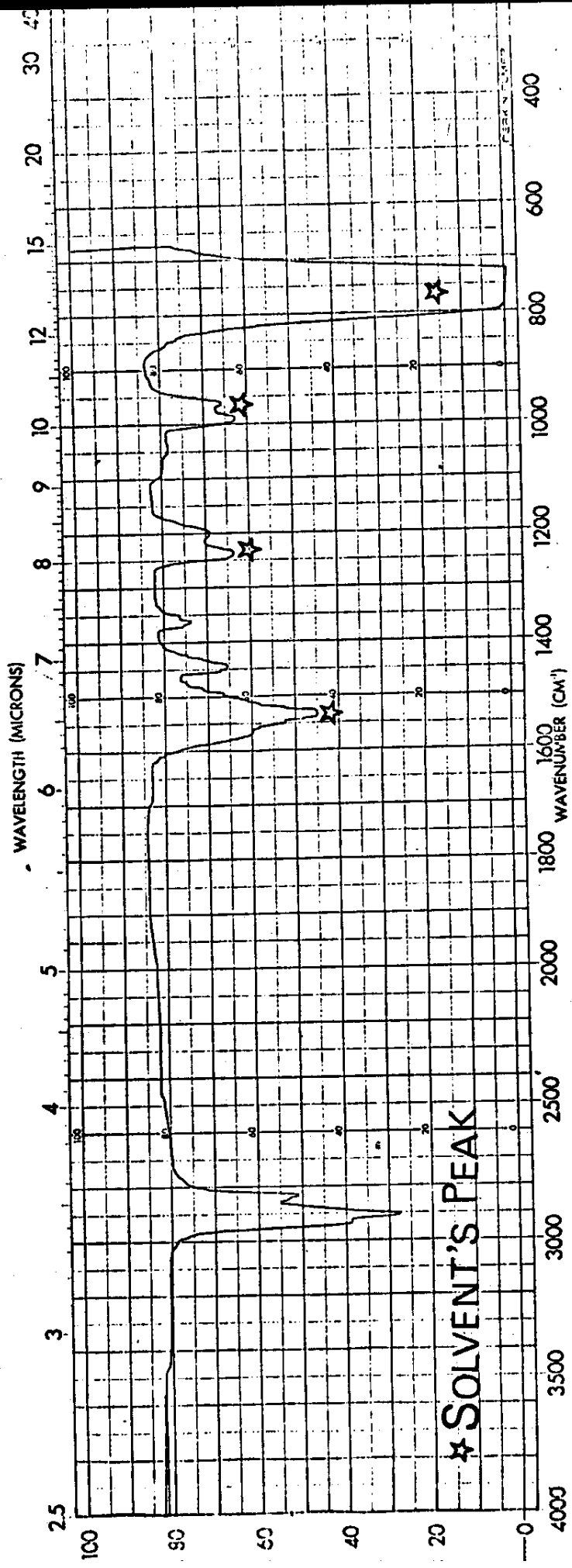


FIGURE 19. INFRARED SPECTRUM OF THE AROMATIC FRACTION OF WHITE ROCKS TARSAND OUTCROP.

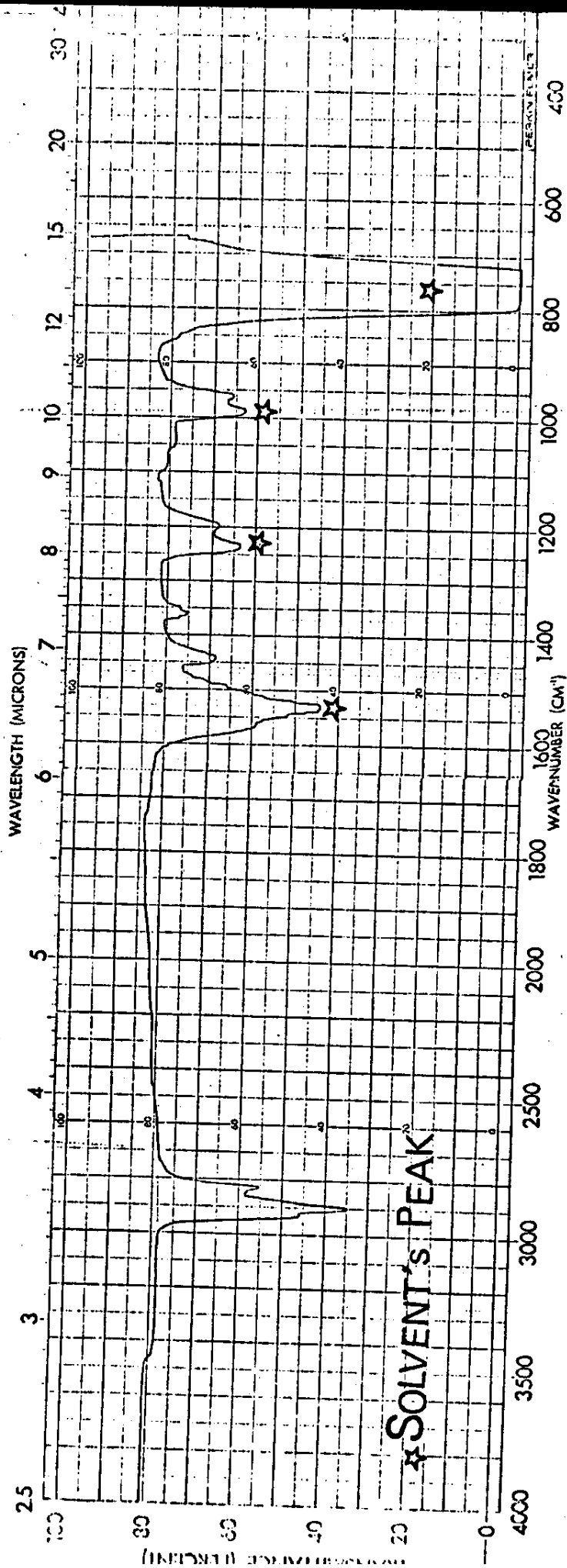


FIGURE 20. INFRARED SPECTRUM OF THE AROMATIC FRACTION OF P.R. SPRING TARSAND OUTCROP.

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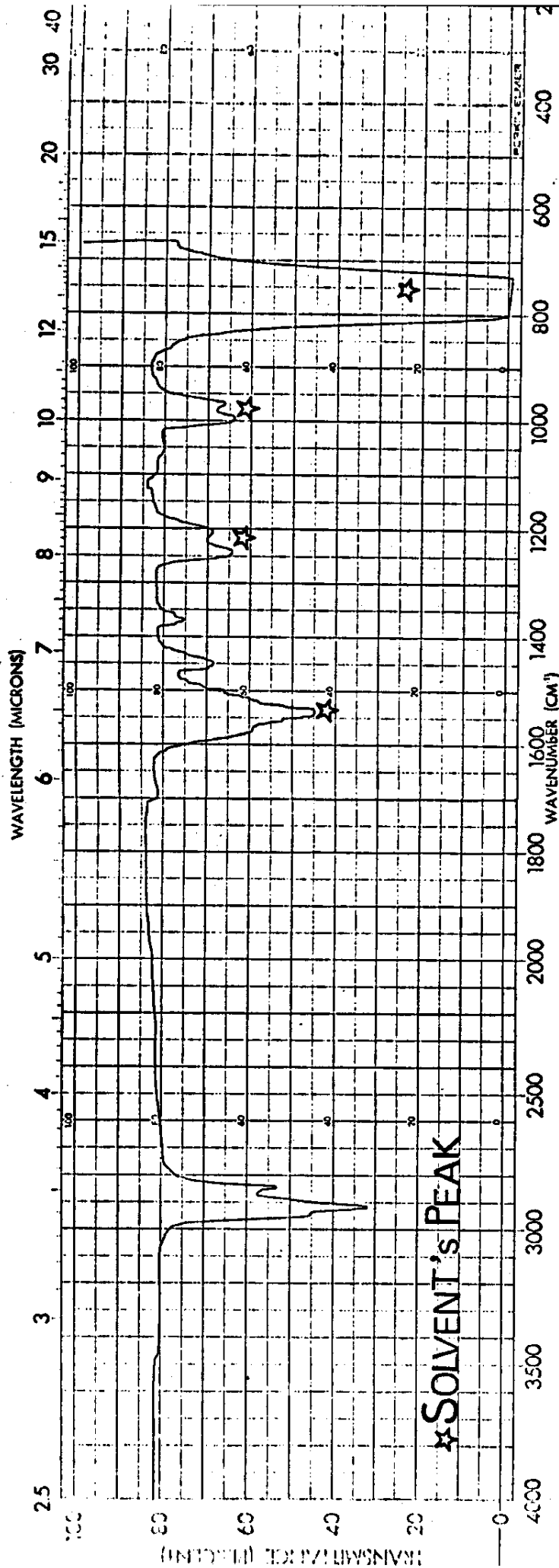


FIGURE 21. INFRARED SPECTRUM OF THE AROMATIC FRACTION OF SUNNY SIDE TARSAND OUTCROP.

## REFERENCES

- Abelson, P. H. and Parker, P. L. (1962) Fatty acids in sedimentary rocks: Carnegie Inst. Wash. year b., Vol. 61, pp. 181-184.
- Anders, D. E., Anderson, P. C., Gardner, P. M., Whitehead, E. V., and Robinson, W. E.: Geochim. Cosmochim. Acta, Vol. 38, p. 1304 (1969).
- Anders, D. E., and Robinson, W. E., (1971) Cycloalkane constituents of the bitumen from Green River shale: Geochim. Cosmochim. Acta, Vol. 35, pp. 661-678, (1971).
- Anders, D. E., Doolittle, F. G., and Robinson, W. E., Analysis of some aromatic hydrocarbons in a benzene soluble bitumen from Green River shale: Geochim. Cosmochim. Acta, Vol. 37, pp. 1213 to 1228, (1972).
- Bonilla, H., Correlation of hydrocarbons in gilsonite, tar sand, Red Wash crude oil, and oil shales from the Green River Formation, Utah and Colorado: M. Sc. Thesis, Colorado School of Mines, T-1672.
- Bradley, W. H., 1966: Geo. Soc. Am. Bull. Vol. 77, p. 1333.
- Burlingame, A. L., Haug, P., Belsky, T., and Calvin, M.: Proc. Nat. Acad. Sci., 54, 1406 (1965).
- Calvin, M., 1969, Chemical Evolution: Oxford University Press, Oxford.
- Donnell, J. R., et al, 1967, Oil shale in the Green River Formation: U. S. Geological Survey, Denver, Colo., P. D. 14 (7).
- Douglas, A. G., and Grantham, P. J. (1973) Fingerprint Gas Chromatography in the Analysis of some Native Bitumen, Asphalts and Related Substances: Organic Geochemistry Unit, Geology Department, Porter Building, The University, New Castle upon Tyne, NE17RU, England.
- Eglinton, G., Scott, P. M., Belsky, T., Burlingame, A. L., and Calvin, M. (1964) Hydrocarbons of biological origin from a one-billion-year-old sediment: Science, Vol. 145, pp. 263-264.

- Eglinton, G., Henderson, W., and Wollrab, V.: Chem. Commun., 710 (1968).
- Gallegos, E. J., Identification of new steranes, terpanes, and branched paraffins in Green River shale by combined capillary gas chromatography and mass spectrometry: Analytical chemistry, Vol. 43, No. 10, August 1971.
- Gallegos, E. J., 1973. Identification of phenylcycloparaffin alkanes and other monoaromatics in Green River shale by gas chromatography and mass spectrometry: Analytical Chemistry, Vol. 45, No. 8, July 1973.
- Han, J., McCarthy, E. D., Hoeven, W. V., Calvin, M., and Bradley, W. H., 1968, organic geochemical studies II. A preliminary report on the distribution of aliphatic hydrocarbons in algae, in bacteria, and in a recent lake sediment: Natl. Acad. Sci. Proc., Vol. 59, pp. 29-33.
- Haug, P., Schnoes, H. K., and Burlingame, A. L. (1967) Iso-prenoid and dicarboxylic acids isolated from the Colorado Green River shale (Eocene): Science 158, pp. 773-773.
- Hills, I. R., Smith, G. W., and Whitehead, E. V. (1968) Hydrocarbons from fossil fuels and their relationship with living organisms: Preprints, Div. of Petroleum Chemistry Inc., Amer. Chem. Soc., Vol. 13, No. 4, pp. B4-B18.
- Johnson, R. W., 1973, Early diagenesis of fatty acids in a salt marsh environment: Geochim. Cosmochim. Acta, Vol. 37, pp. 1943-1955.
- Kvenvolden, K. A. and Peterson, E. (1969) Amino acid enantiomers in Green River Formation oil shale. Abstracts, Ann. Meeting Geol. Soc. Amer., Atlantic City, N.J., 132-133.
- Lawlor, D. L., and Robinson, W. E. (1965) Fatty acids in Green River Formation oil shale. Preprints, Div. of Pet. Chem., Inc., Amer. Chem. Soc. Vol. 10, No. 1, pp. 5-9.
- Leo, R. F. and Parker, P. L., (1966) Branched chain fatty acids in sediments: Science 152, pp. 649-650.

- Meinschein, W. G., 1959, origin of petroleum: Amer. Assoc. Petroleum Geologists, Vol. 43, No. 5, pp. 925-943.
- Morandi, J. R. and Jensen, H. B. (1966) Comparison of porphyrins from shale oil, oil shale, and petroleum by absorption and mass spectroscopy: Chem. Eng. Data, Vol. 11, pp. 81-88.
- Oro, J. and Tornabene, T. G.: J. Bacterial, Vol. 93, p. 1811 (1967).
- Palacas, J. G. (1959) Geochemistry of carbohydrates: Thesis, University of Minn., Minneapolis, Minn.
- Ponnamperuma, C., 1968, Abiogenic hydrocarbons: Preprints, Div. Petroleum Chem. Inc., Am. Chem. Soc., Vol.13, No.4, pp. B21-B22.
- Robinson, W. E., and Cummins, J. J.: J. Chem. Eng. Data, 9, 304 (1964).
- Robinson, W. E., Cummings, J. J., and Dinneen, G. U. (1965) Changes in Green River oil-shale paraffins with depth: Geochim. Cosmochim. Acta, Vol. 29, pp. 249-258.
- Rudakov, G., 1967, Recent developments in the theory of the non-biogenic origin of petroleum: Chem. Geol., Vol. 2, pp. 179-185.
- Schrayer, G. J. (1968) Current views on the origin of petroleum: Preprints, Div. of Petroleum Chemistry Inc., Amer. Chem. Soc., Vol. 13, No. 4, pp. B40-B42.
- Smith, P. V., 1954, Studies on origin of petroleum: Occurrence of hydrocarbons in recent sediments: Amer. Assoc. Petroleum Geologists Bull., Vol. 38, No. 3, pp. 377-404.
- Thiessen, R. 1925: U. S. G. S. Prof. paper, 132, p. 126.
- Thompson, W. D., Williamson, C. R., and Picard, M. D., Petrology Geochemistry and stratigraphy of black shale facies of Green River Formation (Eocene), Uinta Basin, Utah: Utah Geological and Mineralogical Survey, Bulletin 100, June, 1973.