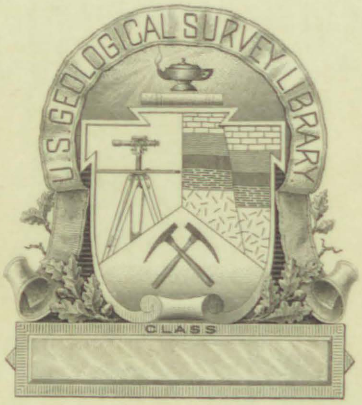
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GENESIS OF OIL IN METALLIFEROUS VEINS,
SAN JUAN MOUNTAINS, COLORADO

By Peter M. Gerrild

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GENESIS OF OIL IN METALLIFEROUS VEINS, SAN JUAN MOUNTAINS, COLORADO

By PETER M. GERRILD

Abstract

A tarry, benzene-soluble material is present in metal-rich veins in the Idarado mine, Ouray, Colo., in an area not known to have petroleum resources. The material was compared chemically, spectrometrically, and chromatographically with oils from four fields in the nearby Paradox basin. Each oil field contains reservoir rocks equivalent to rock units known to extend beneath volcanic rocks near the mine. Carbon and sulfur isotope data and gas chromatographic data indicate a similarity between the oil from the Sierra field and the "oil" from the mine. Thus, the origin of the vein oil from Cretaceous sediments seems both geologically and chemically possible.

Introduction

A viscous dark-brown benzene-soluble oily material seeps from crosscutting metal-rich veins in two tunnels in the Idarado mine, near Telluride, Colo. (fig. 1), in an area not known to have petroleum

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Figure 1.--NEAR HERE

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resources (Fischer and others, 1968). The rock bodies in which these oil seeps occur are separated by as much as 400 feet of volcanic rocks from underlying possible source sediments (J. N. Major, written commun., 1970). Although they are uncommon in this area, such oil-bearing veins in ore bodies have been described before (for example, Bailey and Everhart, 1964, p. 102; Barghoorn, Meinschein, and Schopf, 1965, p. 461). Because there are approximately 50 producing oil fields in the nearby Paradox and San Juan basins, and because some of the same sedimentary formations that produce oil are known to extend beneath the San Juan Mountains, it is of geologic interest and possible economic significance to determine the source and type of oil in the mine. If it can be shown that oil from a particular producing zone in Mississippian, Pennsylvanian, or Cretaceous rocks is similar to that in the mine, a possible route of migration could be outlined, indicating possible reservoir rocks below the San Juan volcanics that could be tested by drilling.

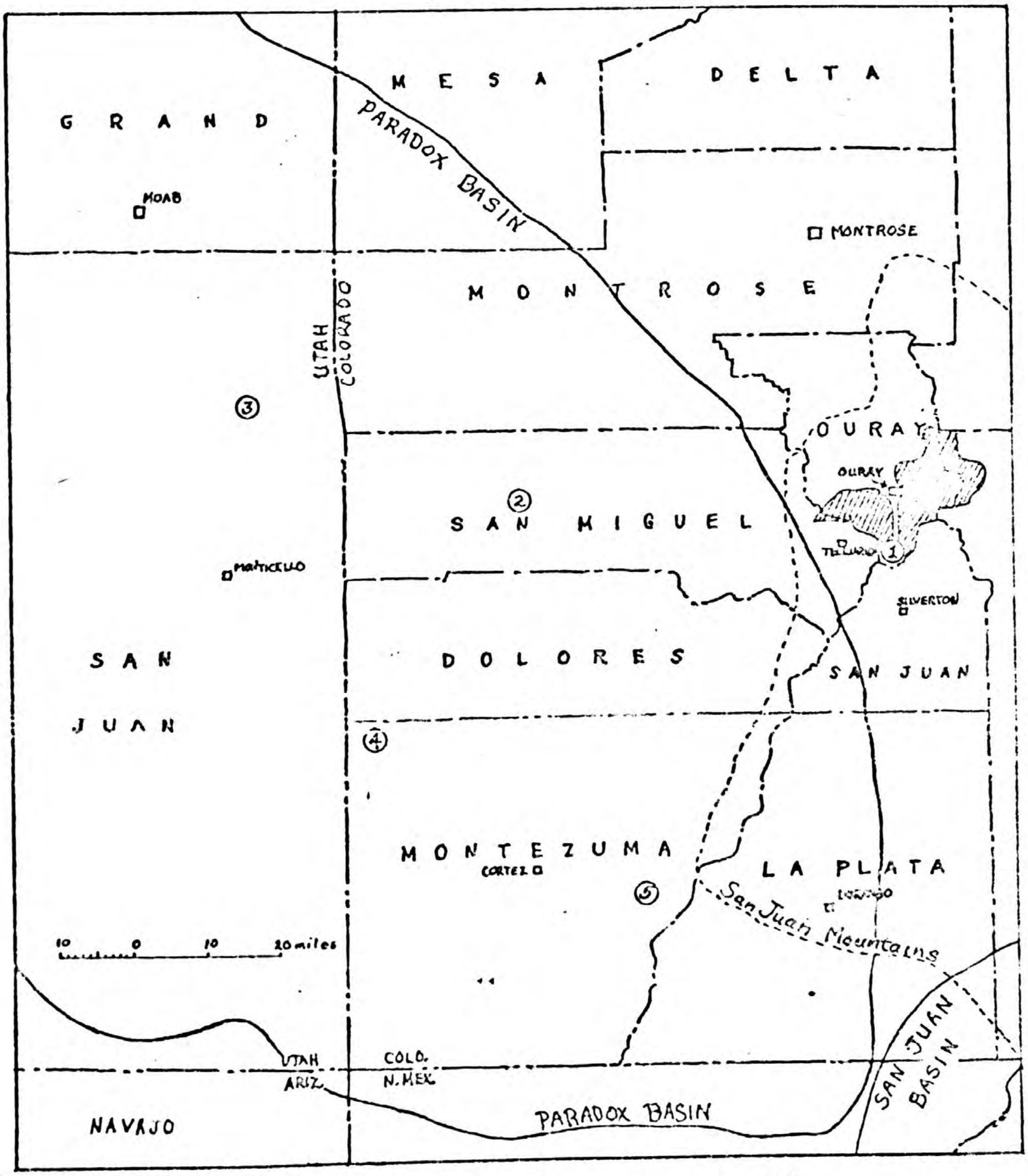

Figure 1. - Map of Four Corners region showing locations of (1) Idarado mine, and (2) Andys Mesa, (3) Lisbon, (4) Papoose Cañon, and (5) Sierra oil fields. Shaded area represents Uncompahgre primitive area

The Idarado mine is in the southern part of the Uncompahgre primitive area, between the towns of Ouray, in Ouray County, and Telluride, in San Miguel County, Colo. (fig. 1). The primitive area is characterized by spectacularly rugged mountains, providing a recreational area for tourists. Numerous old mines and prospects are accessible by trails. Most of the primitive area is between 9,000 and 13,000 feet in altitude, and consists of a domal uplift of rocks that were subjected to intrusive igneous activity three different times, the most recent being in middle to late Tertiary time (Fischer and others, 1968, p. C5). Extensive mineral-rich veins were formed in fissures radiating from the Silverton caldera which developed during the most recent igneous activity, in Late Tertiary time (Burbank, 1941; Burbank and Luedke, 1961). Sedimentary rocks of Precambrian, Paleozoic, Mesozoic, and Cenozoic age crop out in the primitive area (Fischer and others, 1968, p. 5-13). Rocks of Precambrian age generally underlie the primitive area, but are exposed only along the Uncompahgre River and Red Mountain Creek south of Ouray. Paleozoic and Mesozoic rocks pinch out eastward along north-trending zones near the middle of the primitive area. Predominantly volcanic rocks of Cenozoic age, and some intrusives of Late Cretaceous and of Tertiary ages, are the near-surface rocks over most of the primitive area (table 1).

Table 1.--NEAR HERE

Table 1.--Generalized table of rock units in the Uncompahgre primitive area, Colo., (From Fischer and others, 1968.)

Era	Period	Rock units	
Cenozoic	Quaternary	Alluvium, glacial debris, talus, and so on.	
	Tertiary	Intrusive stocks and dikes.	
		Potosi Volcanic Group.	
		Silverton Volcanic Group.	
		San Juan Formation.	
		Telluride Conglomerate.	
	Tertiary or Cretaceous	Intrusive stocks, laccoliths, dikes, and sills.	
Mesozoic	Cretaceous	Mancos Shale.	
		Dakota Sandstone.	
	Jurassic	Morrison Formation	
		Wanakah Formation	"Marl" member.
			Bilk Creek Sandstone Member
			Pony Express Limestone Member.
		Entrada Sandstone.	
	Triassic	Dolores Formation.	
Paleozoic	Permian	Cutler Formation.	
	Pennsylvanian	Hermosa Formation.	
		Molas Formation.	
	Mississippian	Leadville Limestone.	
	Devonian	Ouray Limestone.	
		Elbert Formation.	
Precambrian		Uncompahgre Formation and intrusive dikes and sills.	

It is important to consider the geological likelihood of oil-bearing sediments extending from the Idarado mine to oil fields of the Paradox Basin. The Dakota Sandstone of Cretaceous age, the Hermosa Formation of Pennsylvanian age, and the Leadville Limestone of Mississippian age, all of which contain oil in the Paradox Basin, are found in the Uncompahgre primitive area. The approximate eastern edges of Paleozoic and Mesozoic beds are along a north-trending line through the primitive area (Fischer and others, 1968, fig. 2). J. R. Hillebrand (1968, fig. 1) showed Mesozoic and Paleozoic sediments directly underlying the volcanics of the Montana-Argentine vein of the Idarado mine. Haun and Kent (1965, fig. 6) showed that the Mississippian System was continuous in the southern Paradox Basin. The Leadville Limestone is specifically described by Ohlen and McIntyre (1965, fig. 3) as extending from southeastern Utah, to a point some distance north and east of Durango, Colo., where it is perhaps 50-100 feet thick. Wengerd and Matheny (1958, fig. 17) showed the Honaker Trail Formation to have been continuous between the Ouray area and the southern Paradox Basin. They showed (1958, fig. 15) the Paradox Formation as continuous in the Four Corners region, but with an eastern limit along a line approximately from Naturita, Colo., to Durango, Colo. It has been suggested (R. J. Hite, oral commun., 1971) that the Paradox salt deposits could extend as far east and north as the Uncompahgre primitive area. In the Idarado mine vicinity this part of the Pennsylvanian System is known as the Hermosa Formation (Fischer and others, 1968, p. 8) and has a maximum thickness of about 1,450 feet near Ouray. Young (1960, fig. 4) showed the Dakota Group as continuous in the region of interest. In short, sedimentary rocks that contain oil in four oil fields in the Paradox Basin (fig. 1) appear to be present underground near the mine, and thus are possible sources of the oil extracted from the mine rock.

Acknowledgments

Many people have contributed significantly to this study. The author gratefully acknowledges the helpful suggestions and guidance of Vernon E. Swanson, U.S. Geological Survey, and George B. Lucas, Colorado School of Mines, who helped organize this research and reviewed the results. James G. Palacas, U.S. Geological Survey, gave valuable suggestions for the revision of this manuscript. Frederick S. Fischer, U.S. Geological Survey, supplied the initial mine sample, and, with Robert J. Hite, gave valuable information concerning the geology of the area of study. James N. Mayor, Idarado Mining Co., and Edward A. Schmidt, U.S. Geological Survey, arranged for and helped with the collection of samples. Jerry W. Long, James E. Fassett, and George H. Horn, U.S. Geological Survey, and Velmar O. Gustafson, Union Oil Co., also helped arrange for sample collection. Several Survey employees assisted in the analysis of the samples: James N. Nishi, emission spectrography; James S. Wahlberg, X-ray fluorescence spectrography; Tom G. Ging and Irving C. Frost, elemental analysis; Robert O. Rye, Gary L. Lenz, Irving C. Frost, and Alan A. Roberts, sulfur isotope analysis; Irving Friedman, carbon isotope analysis; and Alan A. Roberts, gas chromatography. William S. Ferguson, Colorado State University, gave helpful suggestions regarding silica-gel chromatography. Without the help of all these people, this study would have been impossible.

Idarado mine sample descriptions

Oil seeps have been observed at several places within the Idarado mine, one of two mines in operation in 1969 in the Uncompahgre primitive area and a major producer of copper, lead, zinc, gold, and silver in Colorado (Fischer and others, 1968, p. C54). Eight sites in the mine were sampled at two different levels in the plane of a major ore vein, known as the Montana-Argentine vein, as shown on figure 2. I collected seven samples from the 2,000-foot level in September 1969. The sample from site no. 8, the one nearest the volcanic-sediment rock interface, was collected in October 1969 by the mine geologist, James N. Mayor, and mailed to the U.S. Geological Survey laboratories in Denver, Colo.

Figure 2.--NEAR HERE

The wall rocks adjacent to the vein where seven of the eight oil samples were taken, at the 2,000-foot level, are tuffs and other volcanic rocks of the San Juan Formation. The eighth sample of oil was collected lower in the mine from a part of the vein where it cuts through the Telluride Conglomerate. At still lower levels in the mine, the vein, which is steeply dipping, intersects Jurassic and Triassic sandstone and limestone that dip about 15 degrees to the north, and unconformably underlie the Telluride conglomerate

Samples of oil-stained and oil-impregnated rock were placed in small plastic bags. No effort was made to refrigerate the samples because the seeps had been exposed for several years.

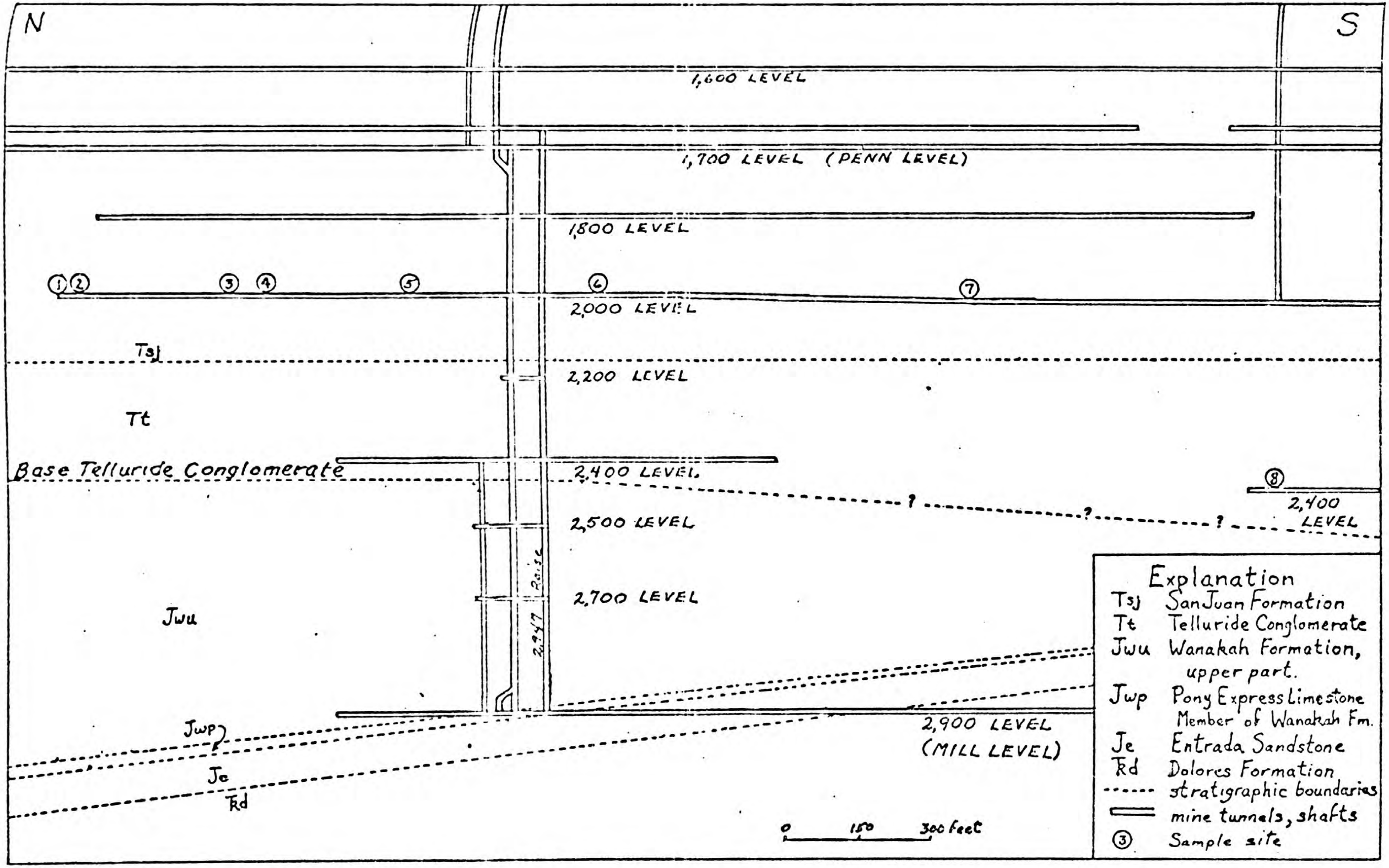

Figure 2.--Longitudinal north-south section of part of Montana-Argentine vein, Idarado mine, showing rock-unit contacts, and sites where oil seeps were sampled. (After Hillebrand, 1968.)

Oil-field sample description

Samples from four producing oil fields nearest the mine (E. A. Schmidt, oral commun., 1970; J. W. Long, written commun., 1970; V. O. Gustafson, written commun., 1970) were collected December 8, 1970. The fields are in the Paradox basin (Fetzner, 1960) of southwestern Colorado and southeastern Utah (table 2). All are approximately

Table 2.--NEAR HERE

50 to 90 air miles from the Idarado mine (fig. 1). Although oil fields nearer the mine were in operation in the past (Wenger and Reid, 1960), none remained in production in 1970. It has been suggested (R. J. Hite, oral commun., 1971) that the oils from the Papoose Canon and Andys Mesa fields are probably not as representative of the Pennsylvanian oils in the Paradox Basin as are other oils from fields in southeastern Utah such as the Aneth and Ismay fields. However, active oil and gas fields in the Paradox and San Juan basins farther than 90 miles from the mine were not considered for this study.

Samples from the four oil fields were collected on December 8, 1970. Edward A. Schmidt, U.S. Geological Survey, recommended sampling sites and assisted in the collection of samples. The sample from the Lisbon field (fig. 1) was taken from a pipeline at the on-site crude-oil plant, and is a composite of crude oils from that field. Samples from the other three fields were taken from storage tanks at individual wells. All oil-field samples were collected in opaque plastic bottles which had been prewashed with benzene and dilute HCl.

Table 2.--Oil-field sample descriptions [1]

Field name	Location	Production zone, (age), and interval	Sample
Andys Mesa	T. 44 N., R. 16 W., San Miguel Co., Colo.	Honaker Trail Formation, Hermosa Group[2], (Pennsylvanian), 6,981-7,776 ft	Gas, condensate
Lisbon	T. 30 S., R. 24 E., San Juan Co., Utah	Leadville Limestone, (Mississippian), 8,652-8,831 ft	Crude oil
Papoose Canon	T. 39 N., R. 19 W., Montezuma Co., Colo.	Desert Creek zone, Paradox Formation, Hermosa Group[2], (Pennsylvanian), 6,257-6,271 ft	Crude oil
Sierra	T. 35 N., R. 13 W., Montezuma Co., Colo.	Dakota Sandstone (Cretaceous) 1,360-1,378 ft	Crude oil

[1] Schmidt, E. A., oral commun., 1970.

[2] Wengerd and Matheny, 1958, p. 2054, (fig. 3).

Oil characterization methods commonly used

Many methods of characterizing crude oils have been tried. One of the oldest and perhaps the most widely used method of analyzing crude oils is the U.S. Bureau of Mines routine method of analysis (Smith and others, 1951). Specific gravity, API gravity, pour point, percent sulfur, percent nitrogen, and Saybolt Universal viscosity are recorded for the whole crude oil, and specific gravity, API gravity, refractive index, specific dispersion, and correlation index are recorded, if possible, on each of 15 fractions collected in a two-stage analytical distillation. The correlation index is a number representing several properties measured on the crude oil or its fractions (Smith, 1940). Many thousands of crude oil samples have been analyzed by this method since it was first implemented about 1923.

Organic sulfur, nitrogen, and oxygen compounds, metallo-organic complexes, and inorganic materials are examples of minor constituents that have been studied (Ball, Haines, and Helm, 1959). Gas chromatography (Gaylor and others, 1964; Brunnock, 1966; Martin, Winters, and Williams, 1963) and mass spectrometry (Van Hoeven and others, 1966) are but two examples of instrument methods that have been used to identify the organic compounds and groups of compounds in crude oil.

Other studies, perhaps of more significance to this study, deal with the application of the results of these and other analytical methods to petroleum geochemistry. Hodgson (1954) found that the ratio of the concentrations of vanadium and nickel in oils of western Canada is characteristic of the age of the reservoir sands. A definite decrease in V/Ni apparently correlates with an increase in age of the oil from Cretaceous to Devonian. Bonham (1956) found no such useful correlation of metal concentrations with producing strata in Oklahoma nor with pools within producing strata. However, a plot of concentration of vanadium or nickel concentrations in Lower Pennsylvanian oils from the Seminole area, Oklahoma, results in contours which closely parallel Lower Pennsylvanian shoreline in the Seminole area, indicating a possible relationship of metal-organic concentrations in oil with the paleogeography of oil-producing strata in general. Sheldon (1967) found a general correlation between the types and concentrations of trace elements in oils and trace elements in shales of Wyoming, lending support to the theory that phosphatic·black shales of the Phosphoria Formation are the source rocks for oils found in Pennsylvanian and Permian rocks several hundred miles distant.

Stone (1967) used U.S. Bureau of Mines correlation index (C. I.) curves, refractive indexes, and infrared-spectroscopic data, as well as carbon and sulfur-isotopic data and V/Ni, ratios to link source rocks with accumulations of oil and gas in the Bighorn Basin, Wyo. Hunt and Forsman (1957) used the U.S. Bureau of Mines Hempel distillation data, correlation indexes, API gravity, and sulfur content to study the stratigraphic distribution of oil in Wind River Basin, Wyo.

Thode and Monster (1970) successfully used sulfur isotopes (^{32}S and ^{34}S) to correlate oils from the rich northern Iraq fields with possible source rocks, seeming to demonstrate vertical migration from Cretaceous rocks through thousands of feet of sediments into Tertiary rocks. Thode and Monster contended (p. 628) that "...considering the wide range of sulfur isotope ratios found for crude oils, the same isotope pattern for two oils in a field would be strong evidence that they are derived from the same source rock, regardless of the reservoir in which they are found."

Stable carbon isotopes (^{12}C and ^{13}C) have been used to postulate mechanisms of petroleum genesis (Silverman and Epstein, 1958; Park and Dunning, 1961; Silverman, 1964; Vinogradov and Galimov, 1970). Silverman (1965), using stable carbon isotopes, postulated a secondary-migration mechanism involving a type of chromatographic separation of crude oil by sediments along the migration path, basing his conclusion on differences in isotopic composition of oil samples taken from a single oil field.

Gas chromatography has found wide use in the characterization of crude oils. Hundreds of organic compounds in the light ends of petroleum have been identified (for example, Martin and Winters, 1959, 1963; Martin, Winters, and Williams, 1963), and excellent analytical distillation data have been produced (for example, Eggertsen and others, 1960; Gaylor and others, 1964; Brunnock, 1966) by gas chromatography. Recently, this powerful tool has been used in combination with mass spectrometry, where the chromatograph separates individual compounds in petroleum from the rest of the mixture and the mass spectrometer then is used to identify the separated compounds (for example, Van Hoeven and others, 1966; MacLeod, 1968, Eglinton and others, 1966, Mathews and others, 1970; Pedersen and Lam, 1970). Gas chromatographic data have been used with trace element concentrations in crude oil to aid in correlating crude oils with closely spaced Pliocene producing zones in the Elk Hills oil field, Calif. (Connor and Gerrild, 1971).

Brenneman and Smith (1958) studied several techniques in an attempt to correlate crude oils with organic material from their most likely source rocks. Extracts from the presumed source rocks were examined by infrared, ultraviolet, and visible spectroscopy, X-ray fluorescence and diffraction spectrometry, and electron microscopy. When these data were compared with similar types of data from the oils, no significant correlations could be made. However, ultraviolet spectroscopic analysis of the aromatic fraction of the organic extract seemed to be the most promising. Barbat (1967) reviewed several correlation techniques, such as carbon and sulfur isotope ratios, nitrogen to carbon ratios, trace elements, chromatographic (liquid-solid) analysis, infrared spectrometry, oil color, specific dispersion, mass spectrometry, and the U.S. Bureau of Mines correlation index (C. I.). He chose the U.S. Bureau of Mines routine analysis data (from which the C. I. is calculated) as the best over-all correlation tool for the study of crude oils, their source rocks, and migration processes primarily because of the large library of open-filed analyses of oils by the U.S. Bureau of Mines.

Oil characterization methods chosen for this study

Choice of methods to be used in this correlation study was limited to those methods adaptable to very small samples, because the total oil in any vein-rock sample from the mine was only a few milliliters. Methods chosen include:

1) Liquid-solid chromatographic analysis, silica-gel stationary phase.
2) Gas-liquid chromatographic (GLC) analysis.
3) Carbon isotopic analysis.
4) Sulfur isotopic analysis.
5) Emission spectrographic analysis for trace elements.
6) X-ray fluorescence analysis for trace elements.
7) Infrared and ultraviolet analysis.

The combination of all of these methods produces data that can characterize the composition of the crude oils and mine extracts.

Because of the small amounts of extractable oil in the mine samples, it was planned that no single extract would be analyzed by all the methods chosen, but rather that different combinations of the extracts of the mine samples would be analyzed by the different methods. It was hoped that the extracts of the different samples could thus be compared successfully with each other and with crude oil from the four fields selected for the study. Table 3 lists the analytical methods for which data are reported for each extract and crude-oil sample.

Table 3.--NEAR HERE

Table 3. Methods of analysis of Idarado mine samples and crude oils from four fields.

Sample	Spectroscopy		Isotope analysis		Chromatography	
	Emission	X-Ray fluorescence	Carbon	Sulfur	Si-gel	GLC
Idarado mine						
No. 1		X				X
No. 2	X	X			X	X
No. 3	X	X		X	X	X
No. 4	X	X				
No. 5	X	X				
No. 6	X			X	X	X
No. 7			X			
No. 8	X	X	X	X		X
Sierra	X	X	X	X	X	X
Lisbon		X	X	X	X	X
Papoose Cañon		X	X	X	X	X
Andys Mesa		X	X	X	X	X

Sample preparation

All mine samples were crushed, using a steel mortar and pestle, prior to solvent extraction. Nonhomogeneity of samples dictated that the extent of crushing be adjusted to allow maximum exposure of the oil for each sample. Some samples contained so much of the oil that crushing was limited by the formation of tarry rock-powder balls. In other samples, rock surfaces were coated with, but not impregnated with, the oil. Such samples generally were crushed to an average particle size of less than 5 mm.

Most of the oil in the mine samples was readily soluble in benzene. A mixture of three parts benzene and one part methanol was also tried in initial extraction experiments, but pure benzene was preferred for the following reasons:

1) Benzene dissolves the organic material from the mine samples readily.
2) Benzene has been used successfully to extract the "bitumen" fraction from recent sediments (Palacas and others, 1972; Ferguson, 1962).
3) Mixed nonpolar-polar organic solvents have been shown to extract more than just the desired organic fraction (Ferguson, 1962; A. H. Love and J. G. Palacas, unpub. data, 1972).

Any inorganic material extracted from the rock would, of course, affect the results of trace-element analyses, and could possibly affect the results of the sulfur isotope study (Thode and Monster, 1970, p. 276).

All samples were extracted by shaking for 22 hours with 2 to 3 ml of redistilled benzene per gram of sample. This process was repeated for all samples until the extracting fluid was colorless or only slightly colored. Normally three extractions were sufficient.

Each benzene extract and crude-oil sample was filtered through Millipore "Solvinert" filters with 0.5μ pore size, using water aspirator vacuum. Several samples were difficult to filter, until a fine fiberglass filter was placed on top of the membrane filter. The oil sample from the Sierra field was very viscous, and impossible to filter before diluting with about an equal volume of benzene and centrifuging at high speed (14,600 X G) for 1 hour. The extract thus separated was again diluted with an equal volume of benzene, after which it was filtered easily. A very fine sediment was separated from the Papoose Cañon oil sample by centrifuging for less than 1 hour at about 2,500 X G, after which the oil was readily filtered.

The benzene extracts and the benzene solution of the Sierra oil were concentrated using a rotary evaporator and water aspirator vacuum pump. During concentration all samples except those from site nos. 6 and 7 were maintained at about 30°C, using an ice-water trap to increase the concentration rate. The two exceptions were maintained at about 65°C, using a cold-water (about 20°C) trap to increase the concentration rate.

Ashing and ash analysis by X-ray fluorescence and emission spectroscopy

The dry-ashing method reported by Horr, Myers, and Dunton (1961) was used in preparing ash samples for trace-element analysis. Samples of mine extract and oil were weighed to the nearest 10 mg in tared 50 ml Vycor crucibles. The samples were ignited and allowed to burn freely until only a black, carbonaceous char remained. It was necessary to warm the more viscous samples on a hot plate to maintain ignition until the char remained. The ashing was completed by heating the partially covered crucibles at 500°C in a muffle furnace for 18 hours. The crucibles were allowed to cool to ambient temperature, and the ash was weighed in the tared crucible to the nearest 0.01 mg.

All ash samples were analyzed by quantitative X-ray fluorescence spectroscopy and by semiquantitative emission spectroscopy. A laser source, well suited to the analysis of the small (less than 10 mg) ash samples, was used in the emission spectrographic analysis. The six-step method described by Horr, Myers, and Dunton (1961) was used for reporting the emission spectrographic results.

Chromatographic analysis

The liquid-solid chromatographic procedure described by Ferguson (1962) was used to separate each sample into three fractions. Each sample was concentrated under a stream of dry nitrogen at 30-35°C. Evaporation was considered complete when the weight of a 100-200 mg sample changed less than about 0.05 mg per minute at ambient temperature. Predictably, the weight loss for the oil samples was greater than that for the rock extracts, especially for the oils from Papoose Cañon and Andys Mesa, which are condensates that are predominantly volatile hydrocarbons, lighter than about $C_{11}H_{24}$. The oil in the mine samples probably lost most, if not all, of these lighter compounds during years of exposure to air in the mine tunnels. Comparisons could not, therefore, be made on the light ends, but this is not considered to be a serious threat to the validity of the study.

The chromatographic column was prepared essentially without modification from Ferguson's (1962) description. Two grades of silica gel were used as the stationary phase--Davidson Chemical Company's Code 950 and Code 70. The Code 950 gel was pre-treated by boiling a slurry of the gel in concentrated nitric acid for 1 hour. The gel was then washed 10-15 times by decantation with distilled water and activated by heating at 225° C in a muffle furnace overnight. After activation, the gel was stored in a screw-cap jar until used. The Code 70 gel, which required no pretreatment with acid, was ground to produce a 40-60 mesh fraction, which was then activated by heating at 225° C. Both gels were used without further treatment, except that the prepared stocks were reactivated at least once every two weeks.

The chromatographic columns were Pyrex glass, 8 mm I. D., packed to a depth of 26 cm, with the lower 13 cm packed with 4 g of Code 950 gel and the upper 13 cm packed with 2.5 g of Code 70 gel. The gels were packed in the columns by pouring a gel-cyclohexane slurry quickly into the column, which had been partly filled with cyclohexane. After pouring the gel-cyclohexane slurry into the column, the gel settled as the cyclohexane flowed through the column. After packing the column, care was taken to insure that the cyclohexane level remained above the top of the gel phase. Air bubbles in the gel phase should be removed because they cause channeling which results in a loss of efficiency in the chromatographic separation process.

A 100-200 mg portion of the concentrated extract of oil was weighed to the nearest 0.01 mg, and then was dissolved in the weighing vessel in about 3 ml cyclohexane for introduction into the top of the column. The weighing vessel was rinsed with about 2 ml cyclohexane and the rinse fluid was added to the top of the column. The first fraction, called the saturated hydrocarbon fraction, was eluted with 20 ml of cyclohexane, added in 5 ml portions; each portion was allowed to drain so that it just covered the top of the gel before the next portion was added. The second fraction, called the aromatic hydrocarbon fraction, was eluted with 20 ml of benzene, added in 5-ml portions. The third fraction, called the asphaltic fraction was eluted with 30 ml of a 50 percent benzene-50 percent methanol mixture, added in 10-ml portions.

The saturated hydrocarbon fraction was collected until the cyclohexane-benzene interface reached the dropping tip of the column, at which time the aromatic-fraction receiver was installed. The aromatic hydrocarbon fraction was likewise collected until the benzene-benzene methanol interface reached the dropping tip, at which time the asphaltic-fraction receiver was installed. The asphaltic fraction was collected until the top of the final portion of benzene-methanol had passed the top of the gel.

All solvents had been redistilled and stored in glass prior to use. The solvents were evaporated from each of the three eluates under a stream of dry nitrogen. The eluates were then weighed to the nearest 0.01 mg.

All saturated hydrocarbon (alkane) fractions were subjected to GLC analysis. Because of their inherent stability in chemical and metabolical reactions, alkanes have been widely studied in organic geochemistry. Some normal alkanes and some isoprenoid alkanes, notably pristane (2, 6, 10, 14 - tetramethylpentadecane) and phytane (2, 6, 10, 14 - tetramethylhexadecane), are extensively used as possible indicators of the biologic origin of petroleum (Meinschein, 1969, p. 346, 353).

The concentration of each sample was adjusted to about 50 mg/ml with reagent-grade carbon disulfide. The chromatographic columns were 6 feet long, 1/8 inch O. D. stainless steel tubes packed with 100 to 120 mesh Chromosorb W-HP coated with 3 weight-percent SE-30. The helium carrier gas-flow rate was maintained at 40 cc per minute. The column temperature was maintained at 100° C for 1 minute following injection, and was then programmed upward to 300° in 20 minutes (6-2/3° C per minute), and held at this temperature until all peaks were eluted. A Beckman GC-4 gas chromatograph equipped with dual columns and dual hydrogen-flame ionization detectors was used. The recorder was a Beckman 10-inch linear strip-chart recorder equipped with Disc integrator. All chromatograms were recorded at a chart speed of 0.5 inch per minute.

Parts of the saturated hydrocarbon fractions were separated further, using a molecular sieve, to remove the n-alkane molecules from the branched and cyclic alkanes. A Linde 5A molecular sieve, in the form of 1/16-inch pellets, was rigorously conditioned at 195°C at about 3 mm Hg pressure for 3 days to remove traces of water. It was found that conditioning the molecular sieve for only 1 day under these conditions was not long enough and resulted in incomplete removal of the n-alkane fraction. The sieve was stored in a vacuum desiccator until used. A cyclohexane solution of about 20 mg of saturated hydrocarbon fraction was placed in a 3-ml screw-cap vial (with a tin-foil liner in the cap), to which about 2 g of molecular sieve was quickly added from the desiccator. Just enough cyclohexane to cover the molecular sieve was added immediately. The vial was tightly capped and allowed to sit at ambient temperature (about 23°C) for at least 6 days before analyzing the supernatant "branched-cyclic" fraction by GLC. The details of this procedure are herein emphasized because it has been difficult to reproduce results, especially where the procedure needed to be scaled down from gram to milligram quantities. The exact limits of the precautionary measures have not yet been determined, but the above procedure was definitely sufficient for the five samples (from the four oil fields and Idarado mine site no. 8) so analyzed for this study.

Carbon isotope analysis

Filtered samples of the four crude oils and one extract from a mine sample were submitted to Irving Friedman, U.S. Geological Survey, for stable carbon isotope analysis by mass spectrometry. Benzene added to two of the samples (Sierra oil and mine-sample extract) was evaporated thoroughly before analysis. The carbon in the oils was oxidized to CO_2 in the presence of hot copper oxide in a high-vacuum system designed to allow complete conversion of CO to CO_2, and subsequent isolation of CO_2 from other gases present. The mass spectrometer employs a double collecting system, allowing the rapid comparison of mass 45 ($^{13}C^{16}O^{16}O$) and 44 ($^{12}C^{16}O^{16}O$), and a dual inlet allowing rapid switching between standard and reference CO_2. Degens (1969, p. 305-307) summarizes details of sample preparation and instrumental analysis. Analytical results are expressed as deviations between the $^{13}C/^{12}C$ ratio of the sample and $^{13}C/^{12}C$ ratio of the Peedee belemnite (PDB) standard (Silverman and Epstein, 1958). The deviations, expressed as δ-values are calculated as follows:

$$\delta\,^{13}C\text{, in per mil } (^{o}/oo) = \frac{\left(^{13}C/^{12}C\text{ sample} - {}^{13}C/^{12}C\text{ standard}\right)\left(1000\right)}{^{13}C/^{12}C\text{ standard}}$$

Sulfur isotope analysis

The filtered crude-oil samples and the benzene extracts from mine samples were tested for the presence of free sulfur by stirring with a clean, bright copper strip. Darkening of the copper, caused by formation of copper sulfide, was not observed in any of the samples after 3 minutes of stirring of 2-ml portions of each sample with the copper strip. A test solution of about 0.01 percent sulfur dissolved in benzene caused noticeable darkening of the copper strip after 3 minutes of stirring. This comparison indicates that the free sulfur in the undiluted oil samples from the Lisbon, Papoose Cañon, and Andys Mesa fields was much less than 0.5 percent by weight. The amounts of free sulfur in the diluted extracts of mine samples and of the oil sampled from the Sierra field are not as easily estimated, but the amounts are also probably less than 0.5 percent.

The preparation of samples for sulfur isotope analysis included the following steps:

1) Combustion of the sample in a Parr oxygen bomb under 30 atmospheres oxygen.
2) Oxidation of combustion products with bromine water.
3) Precipitation of the produced sulfates as barium sulfate; samples are stored in this form until they are analyzed.
4) Reduction of the barium sulfate to barium sulfide by heating in the presence of carbon.
5) Precipitation of the sulfide as silver sulfide.
6) Collection of sulfur dioxide gas after the silver sulfide is oxidized in the presence of cupric oxide.

Mass spectrographic analysis was made on the collected sulfur dioxide by Robert O. Rye and Gary L. Lenz, U.S. Geological Survey, to determine the ratio of ^{34}S to ^{32}S, which is compared to the ratio from a standard sulfur source, Canyon Diablo troilite (Thode and Monster, 1970). The results are expressed as δ -values, and are calculated in a manner similar to the calculation for carbon-isotope δ-values:

$$\delta\ ^{34}S\text{, in per mil } (^{o}/oo) = \frac{\left(^{34}S/^{32}S \text{ sample} - {}^{34}S/^{32}S \text{ standard}\right)\left(1000\right)}{^{34}S/^{32}S \text{ standard}}$$

Infrared and ultraviolet analysis

Solutions of several saturated hydrocarbon fractions were submitted to Dr. George B. Lucas, Colorado School of Mines, for analysis by infrared and ultraviolet spectroscopy. These analyses were performed mainly to ascertain the purity of the saturated hydrocarbon fractions prior to their analysis for GLC and further separation by molecular sieve adsorption. Initial separations by silica-gel chromatography of the extracts from the mine samples resulted in highly colored saturated hydrocarbon fractions which were shown to contain significant amounts of aromatic hydrocarbons. Additional runs of the extracts through silica-gel columns, however, resulted in clear separation of the fractions.

Discussion of analytical results

Carbon isotope data

The stable carbon isotope data (table 4) suggest that the oils from two oil fields may be related to the oily material in the mine samples. Oils from the Sierra and Lisbon fields with $\delta^{13}C$ values of -29.0 and -26.2 per mil, respectively, have nearly the same values as the extracts from the two mine samples analyzed averaging -27.3 per mil, with a total range of less than 3 per mil. Oils from these three locations are within the range of values for most Mississippian and Devonian oils (Degens, 1969, p. 319). Silverman (1965, p. 57) noted a greater variation, 4 per mil, for three oil samples taken from a single field.

Table 4.--NEAR HERE

Table 4.--Carbon and sulfur isotope data

Sample	$\delta^{13}C$, °/oo [1]	$\delta^{34}S$, °/oo [2]
No. 3	---	-5.77
No. 6	---	-5.40
No. 7	-26.3	---
No. 8	-28.3	-5.16
Sierra	-29.0	-5.80
Lisbon	-26.2	+12.56 [3]
Papoose Cañon	-51.6	-4.60
Andys Mesa	-48.1	[4]

[1] Analyst: Irving Friedman, U.S. Geological Survey

[2] Analysts: Robert O. Rye and Gary L. Lenz, U.S. Geological Survey

[3] Average of two determinations

[4] Insufficient sample for analysis

The oil samples from the Papoose Cañon and Andys Mesa fields are isotopically very light, with $\delta^{13}C$ values of -51.6 and -48.1 per mil, respectively, owing to the high percentage of light (C_1 to C_8) hydrocarbons in the oils (Silverman, 1964, p. 98-99; Silverman and Epstein, 1958, p. 1004; and Vinogradov and Galimov, 1970, p. 223). However, even without the light hydrocarbons, these two oils would probably be isotopically lighter than the oils from the Sierra and Lisbon fields and the extracts from the mine samples.

The carbon isotope analyses of six samples thus indicate that the oil in the veins of the Idarado mine is similar to the crude oil from Cretaceous rock in the Sierra field or from Mississippian rock in the Lisbon field.

Sulfur isotope data

The extracts from three Idarado mine samples and three of the crude-oil samples, from the Sierra, Lisbon, and Papoose Cañon fields were subjected to sulfur isotope analysis by mass spectrometry (table 4). All attempts to isolate sulfur compound derivatives from the Andys Mesa crude oil failed, indicating that such compounds were probably absent from this crude oil.

The $\delta^{34}S$ values for the mine extracts have a very narrow range, -5.16 to -5.77 per mil, averaging -5.44 per mil. The $\delta^{34}S$ values of the oils from the Sierra and Papoose Cañon fields, -5.80 and -4.60 per mil, respectively, are close to the values of the extracts from the mine samples. However, the $\delta^{34}S$ value of the oil from the Lisbon field, +12.56 per mil, is significantly different from the $\delta^{34}S$ values of the extracts from the mine samples. Thus, these sulfur isotope data suggest that the oil in the veins of the Idarado mine may have originated from the same source as the oil from Cretaceous rock in the Sierra field and from Pennsylvanian rock in the Papoose Cañon field.

Silica-gel chromatographic data

Silica-gel chromatographic data are presented for extracts of three mine samples, and crude-oil samples from each of the four oil fields (table 5). Although there is little variation in composition among the three extracts from the mine samples, and among the crude-oil samples, the composition of the extracts is markedly different from that of the crude oils. The average percentage of saturated hydrocarbons in the extracts from the mine samples is 34.8 percent, while that for the crude oils is much higher, 80.4 percent. Conversely, the extracts from the mine samples have a high content of aromatic hydrocarbons and asphaltic compounds, averaging 47.9 and 17.3 percent, respectively, compared with the 16.9 and 2.5 percent, respectively, for the crude-oil samples. These data indicate that if the oil in the

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Table 5.--NEAR HERE

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mineralized veins of the Idarado mine had an origin in common with the crude oil from any of the four fields, Andys Mesa, Lisbon, Papoose Cañon or Sierra, the composition has been greatly modified. Much of the saturated hydrocarbon fraction in the mine extracts might have been converted to aromatic hydrocarbons and asphaltic compounds, or it might have been separated from the aromatic and asphaltic compounds. These changes could have occurred during the migration of oil upward along the vein from the potential sedimentary source rocks beneath the Idarado mine.

Table 5.--Silica-gel chromatographic data

Sample	Saturated hydrocarbons, percent	Aromatic hydrocarbons, percent	Asphaltic fraction, percent
Idarado Mine			
No. 2	33.9	49.9	16.2
No. 3	26.2	54.6	19.2
No. 6	44.2	39.2	16.6
Sierra	79.1	16.3	4.5
Lisbon [1]	70.7	27.1	2.2
Papoose Cañon	83.1	14.8	2.1
Andys Mesa	89.0	9.6	1.4

[1] Average of two determinations.

Gas-liquid chromatographic data

The distribution of total saturated, branched, and cyclic hydrocarbon compounds in extracts from some of the mine samples and in samples of crude oil from four oil fields are shown by the gas-liquid chromatographic data (figs. 3-16).

The distributions of saturated hydrocarbons in the Papoose Cañon crude oil (fig. 4) and the Lisbon crude oil (fig. 5) are nearly identical, with maximum concentration of compounds in the C_{13} to C_{15} region. The distribution of saturated hydrocarbons in the Sierra crude oil (fig. 6) is similar to the distribution in the Papoose Cañon and Lisbon oils, except the maximum concentration of compounds is in the C_{16} to C_{19} range. All three of these crude oils have significant concentrations, as much as 20 to 30 percent of saturated hydrocarbons, in the C_{20} to C_{36} region. The distribution of saturated hydrocarbons in the Andys Mesa crude oil (fig. 3) is markedly different from the distribution in the other three crude oils. The maximum concentration of compounds is in the C_{11} region, and compounds heavier than C_{20} are present only in trace amounts. Some light hydrocarbon compounds were no doubt lost during the collection and preparation of the crude oil samples for gas-liquid chromatographic analysis. This effect would probably be most noticeable in the Andys Mesa crude oil, a gas condensate, which originally had a maximum concentration of compounds probably in the C_4 to C_8 region.

Figures 3, 4, 5, and 6.--NEAR HERE

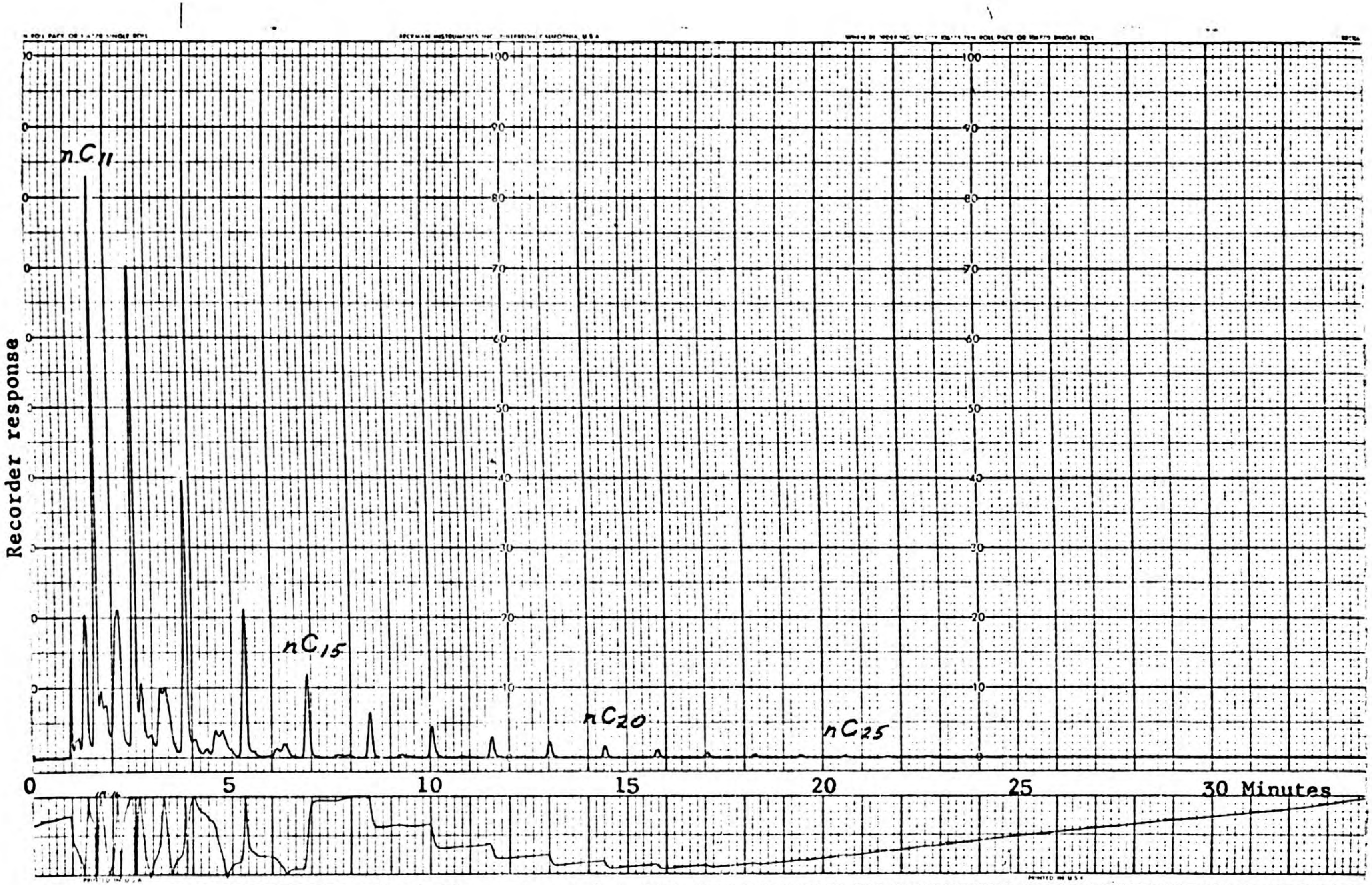

Figure 3. - Gas chromatogram of Andys Mesa oil, saturated hydrocarbon fraction

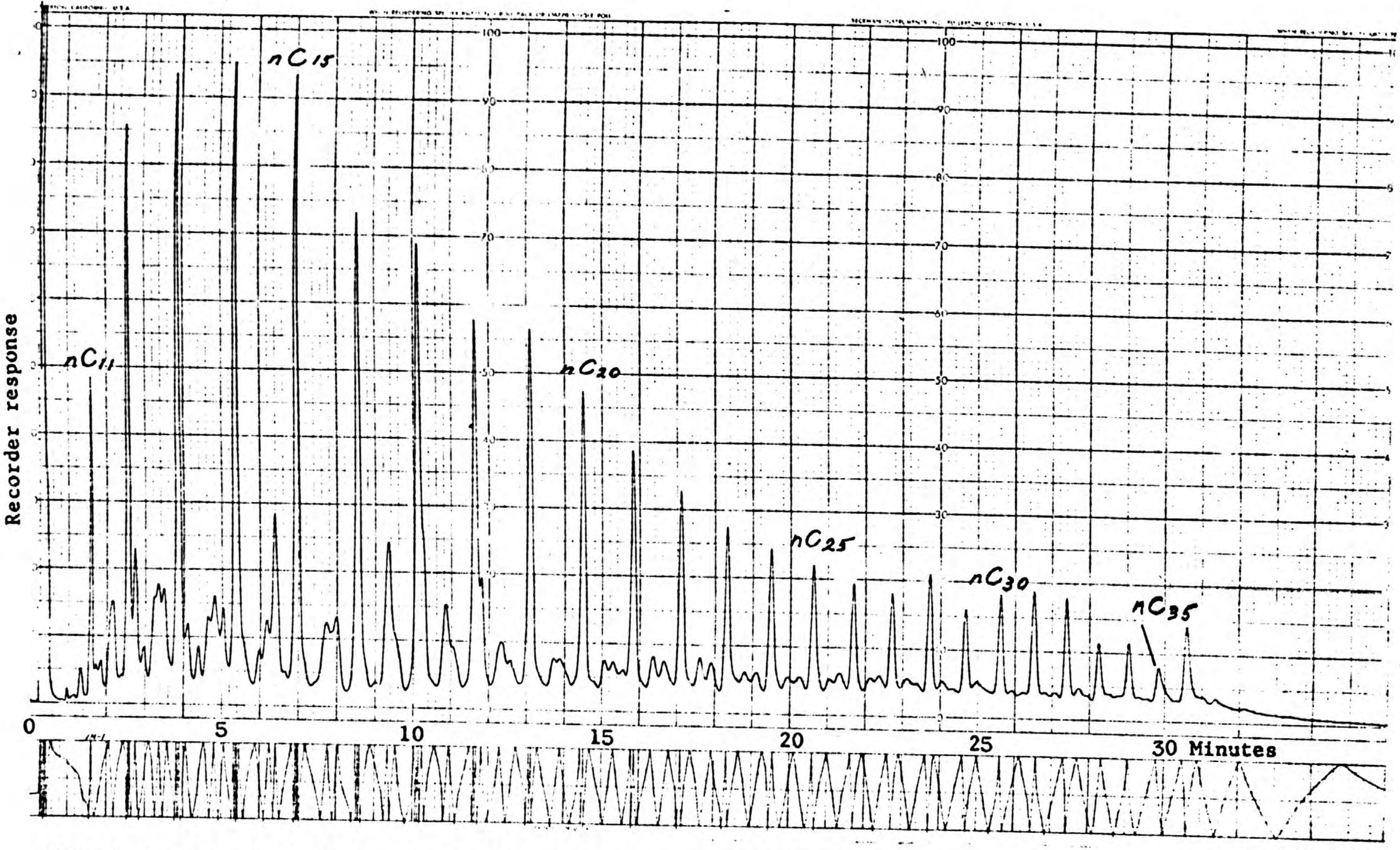

Figure 4. - Gas chromatogram of Papoose Cañon oil, saturated hydrocarbon fraction

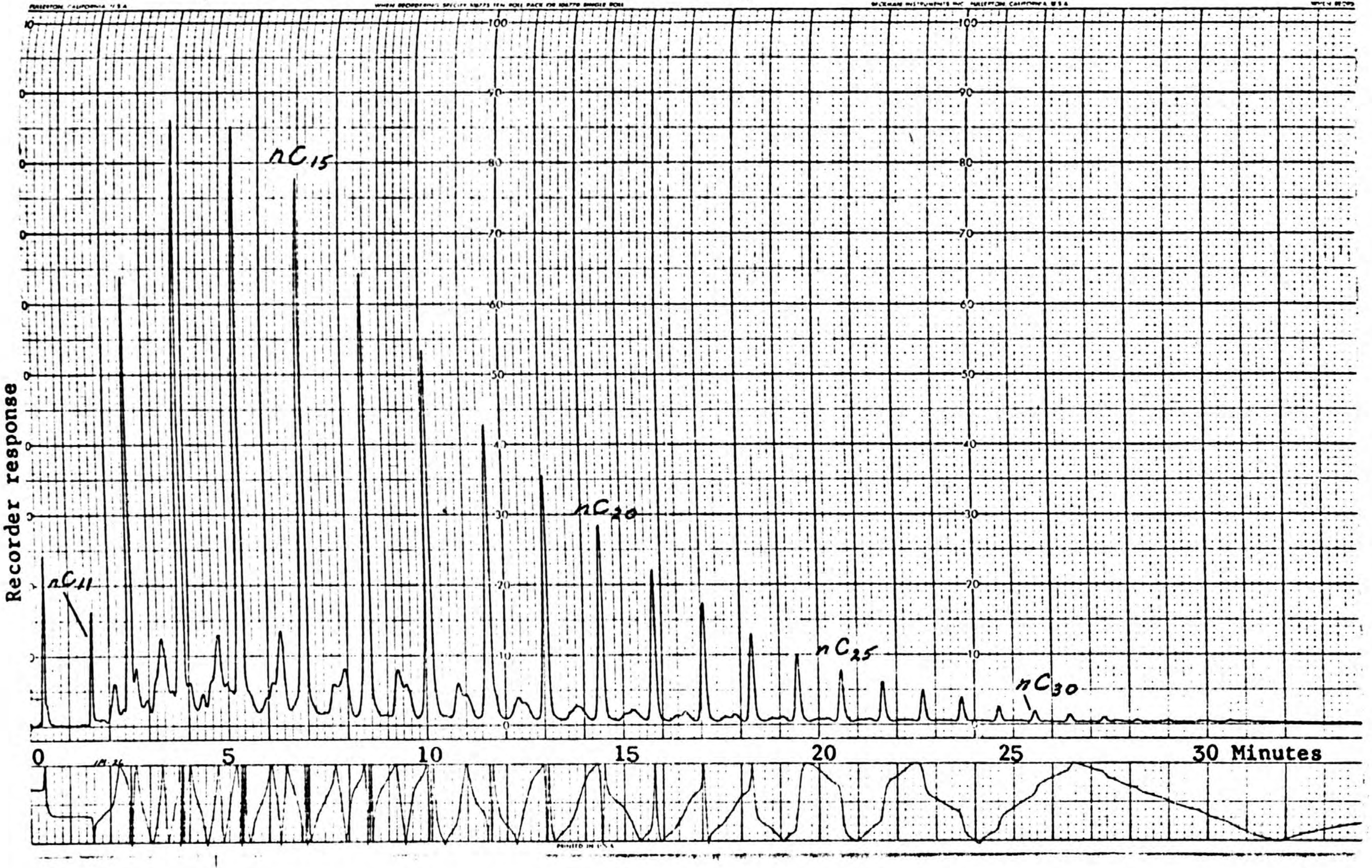

Figure 5. - Gas chromatogram of Lisbon oil, saturated hydrocarbon fraction

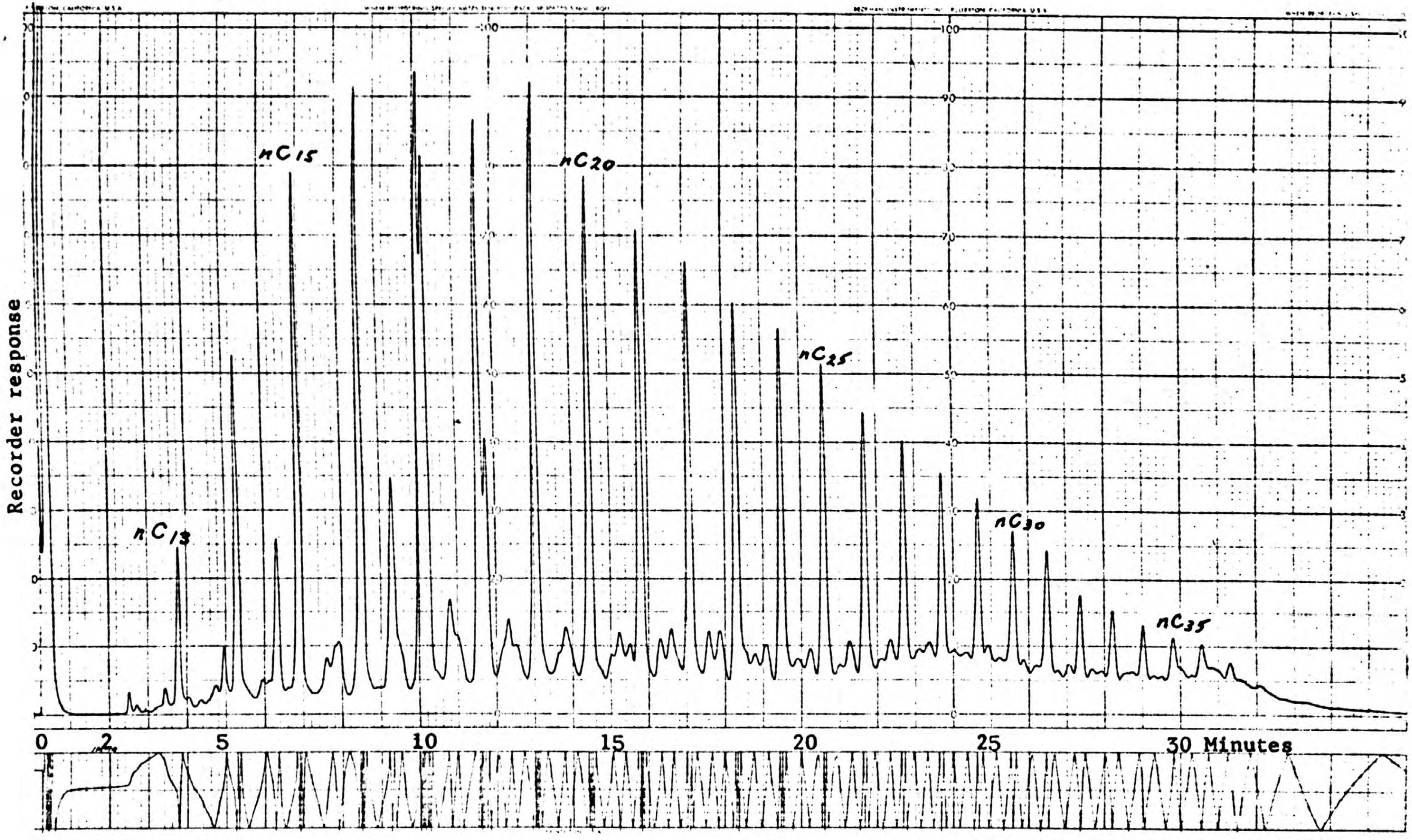

Figure 6. - Gas chromatogram of Sierra oil, saturated hydrocarbon fraction

The n-alkane compounds are the most abundant molecular species in the saturated hydrocarbon fractions of the crude oils, ranging from about 50 percent of the saturated hydrocarbons in the Sierra and Papoose Cañon oils, to about 70 percent in the Andys Mesa oil. Other molecular species present in the saturated hydrocarbon fractions include branched and cyclic alkanes.

The extracts from the mine samples no. 1 (fig. 7), no. 2 (fig. 8), and no. 3 (fig. 9) have nearly identical distributions of saturated hydrocarbons, with a maximum concentration in the C_{28} (about 24 min. retention time) region, and a range from about C_{18} through approximately C_{40}. The chromatographic patterns for these samples indicate that the n-alkane compounds are present only in minor amounts, probably less than 5 percent, and that the dominant molecular species are the branched and cyclic alkanes. The chromatographic patterns of the extracts from mine samples no. 6 (fig. 10) and no. 8 (fig. 11) are quite different from the patterns of nos. 1, 2, and 3 in that the first two show significant amounts of n-alkanes, about 15 to 20 percent in no. 6, and about 50-60 percent in no. 8.

Figures 7, 8, 9, 10, and 11.--NEAR HERE

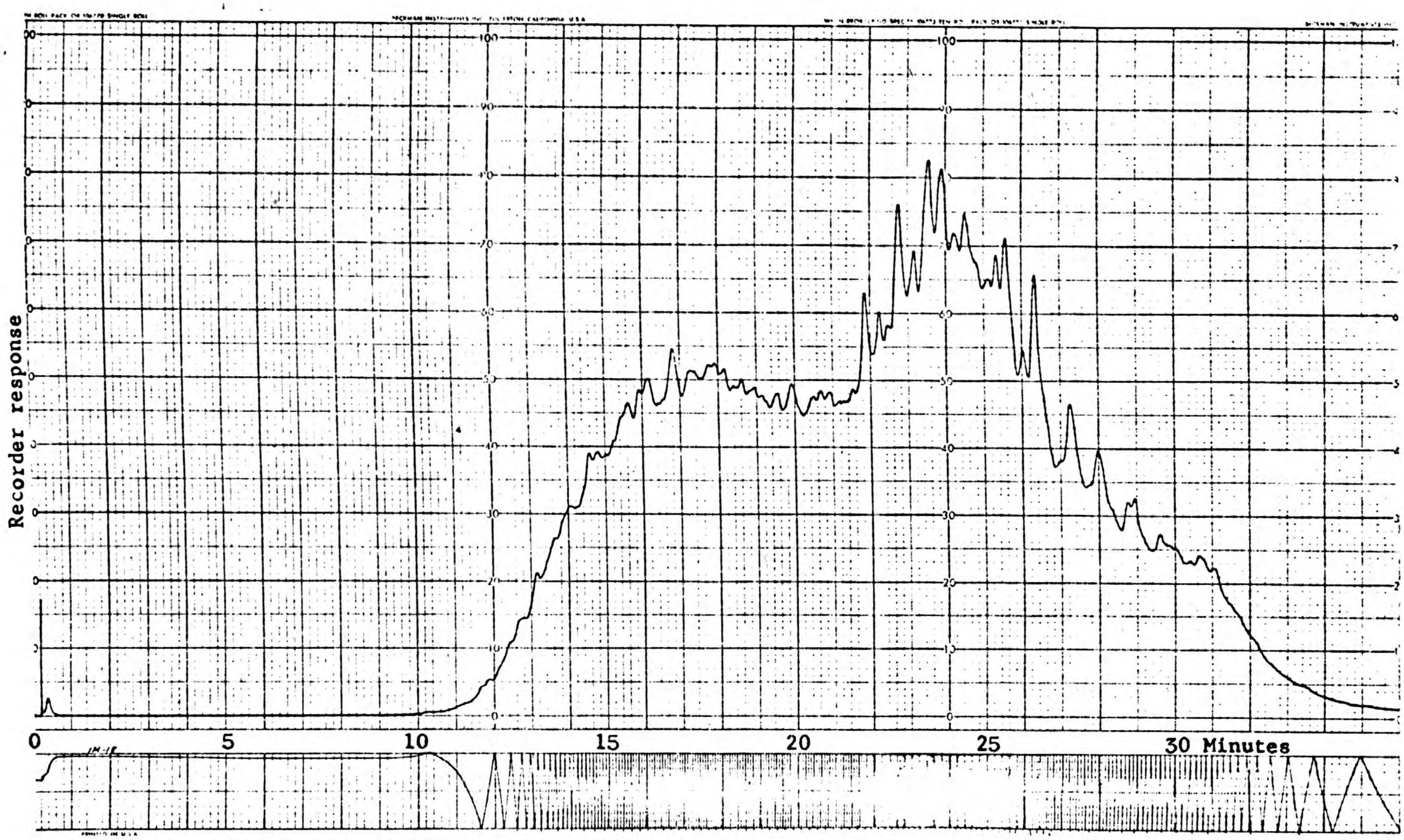

Figure 7. - Gas chromatogram of Idarado mine sample no. 1, saturated hydrocarbon fraction

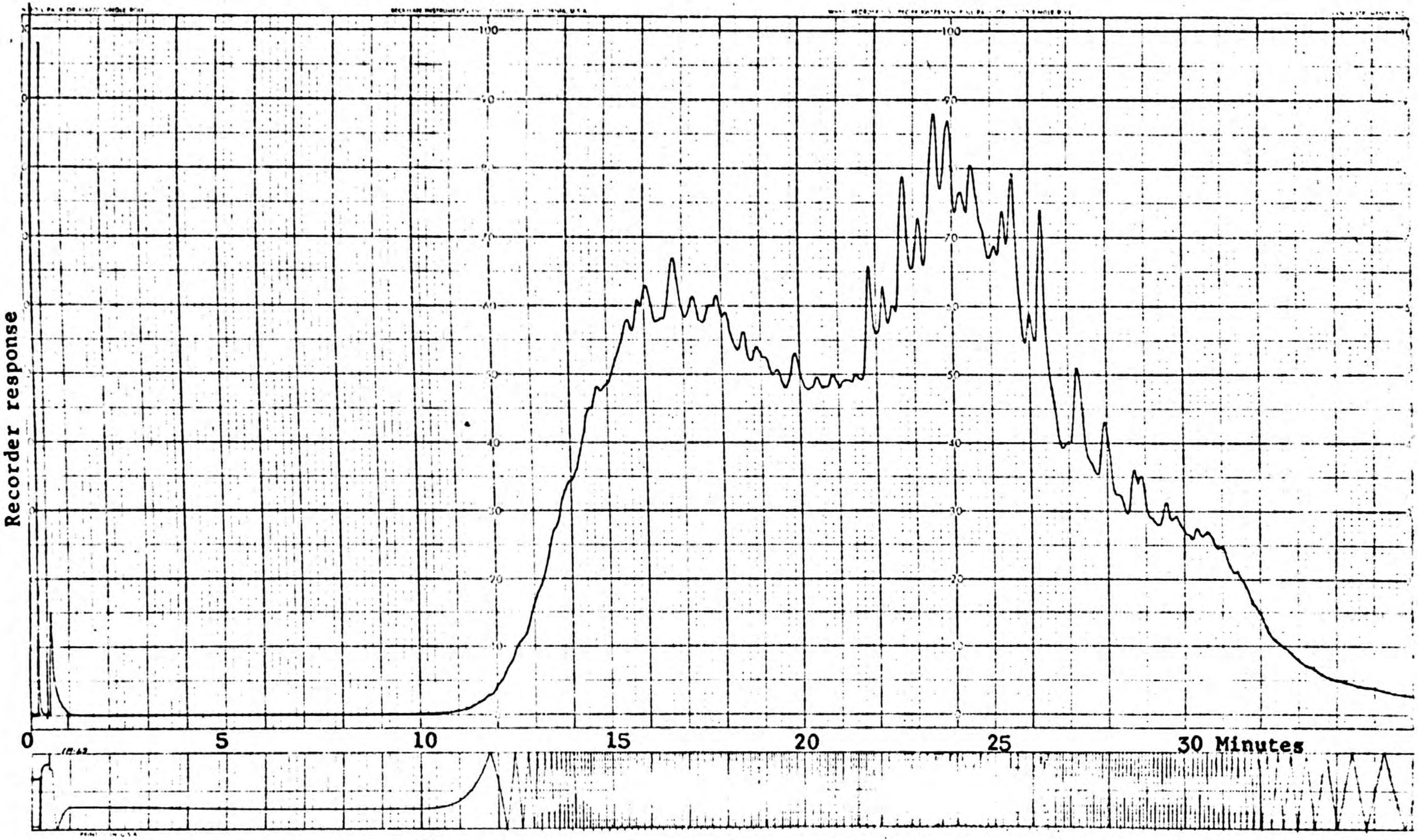

Figure 8. - Gas chromatogram of Idarado mine sample no. 2, saturated hydrocarbon fraction

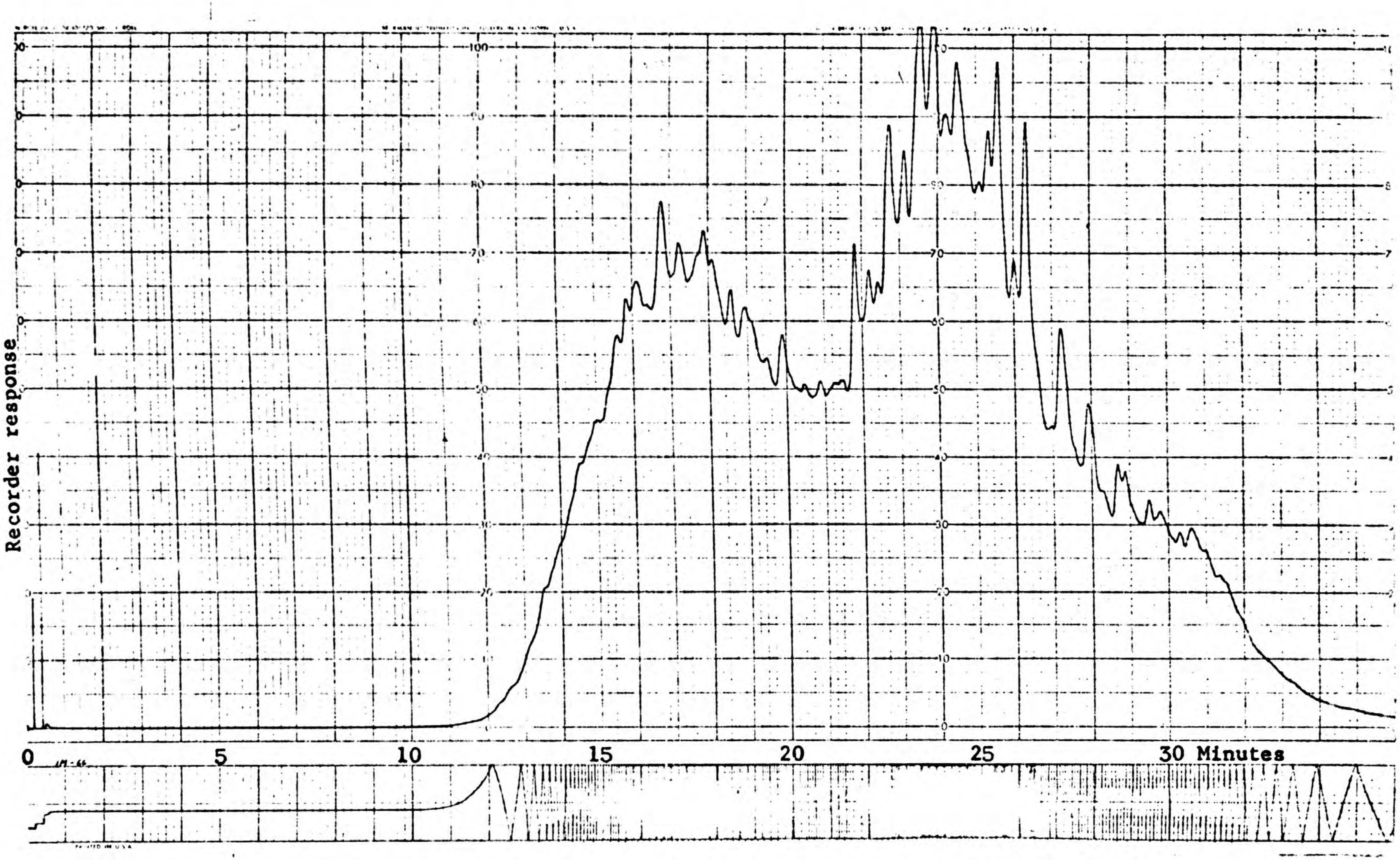

Figure 9. - Gas chromatogram of Idarado mine sample no. 3, saturated hydrocarbon fraction

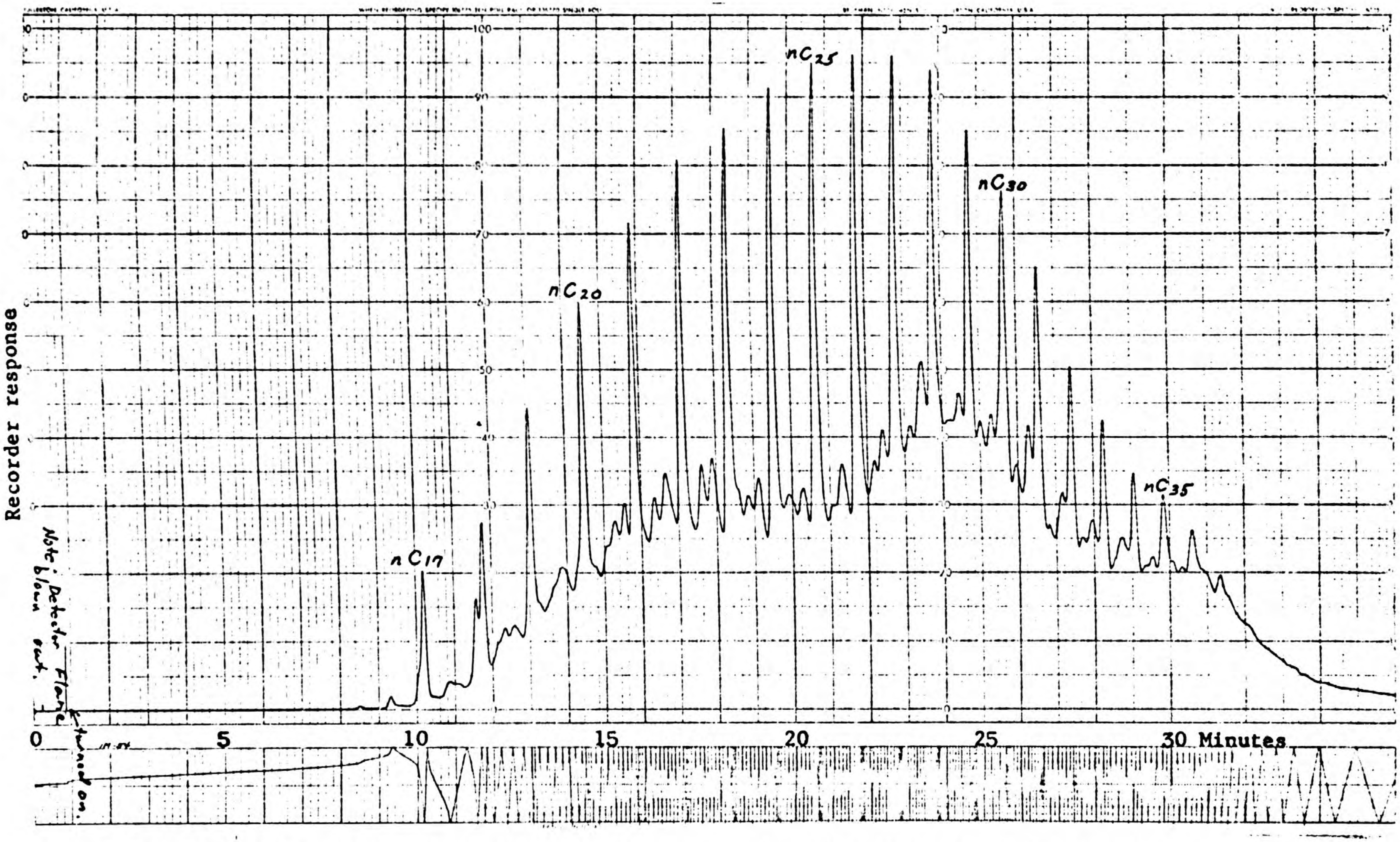

Figure 10. - Gas chromatogram of Idarado mine sample no. 6, saturated hydrocarbon fraction

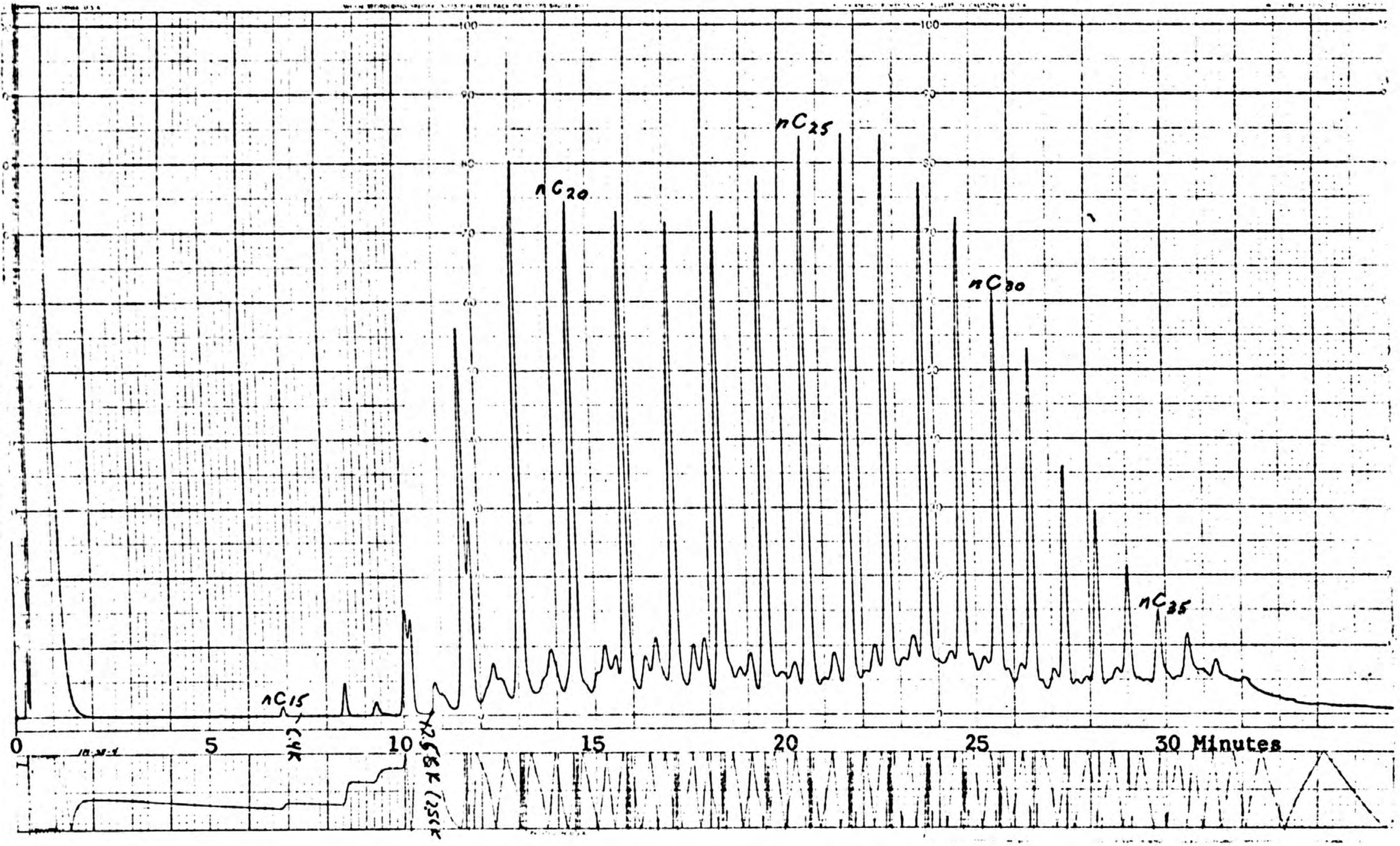

Figure 11. - Gas chromatogram of Idarado mine sample no. 8, saturated hydrocarbon fraction, after fourth silica-gel chromatographing

Because of the similarity between the distribution of saturated hydrocarbons in the extract from mine sample no. 8 (fig. 11) and in the crude-oil samples (figs. 3-6), mine sample no. 8 was chosen for further comparison with the crude oils. Parts of the saturated hydrocarbon fractions of the crude oils and the extract from mine sample no. 8 were passed through a molecular sieve in order to remove the n-alkane molecules, allowing a better comparison of the branched and cyclic hydrocarbons in these samples.

The chromatograms for these branched and cyclic hydrocarbon fractions (figs. 12-16) indicate a general similarity in composition of compounds heavier than about C_{20} (retention times greater than about 14 min.). Of particular interest, however, is the group of compounds with retention times between 9 and 12 minutes. The chromatograms of the extract of the mine sample no. 8 (fig. 16) and of the crude oil from the Sierra field (fig. 15) both have large peaks at 10.4 and 11.8 minutes. These peaks probably represent pristane (10.4 min.) and phytane (11.8 min.), known isoprenoid constituents of many crude oils (Eglinton and others, 1966; Meinschein, 1969; Eisma and Jurg, 1969: Palacas and others, 1972). These two peaks are absent, or are not as large, relative to their neighboring peaks, in the chromatograms of the other three crude oils (figs. 12-14). Thus, on the basis of the similarity between the gas-liquid chromatographic data, the oil from the Idarado mine is similar to the crude oil produced from the Cretaceous rock in the Sierra field.

Figures.--12, 13, 14, 15, 16 NEAR HERE

Figure 12. - Gas chromatogram of Andys Mesa oil, branched-cyclic saturated hydrocarbon fraction

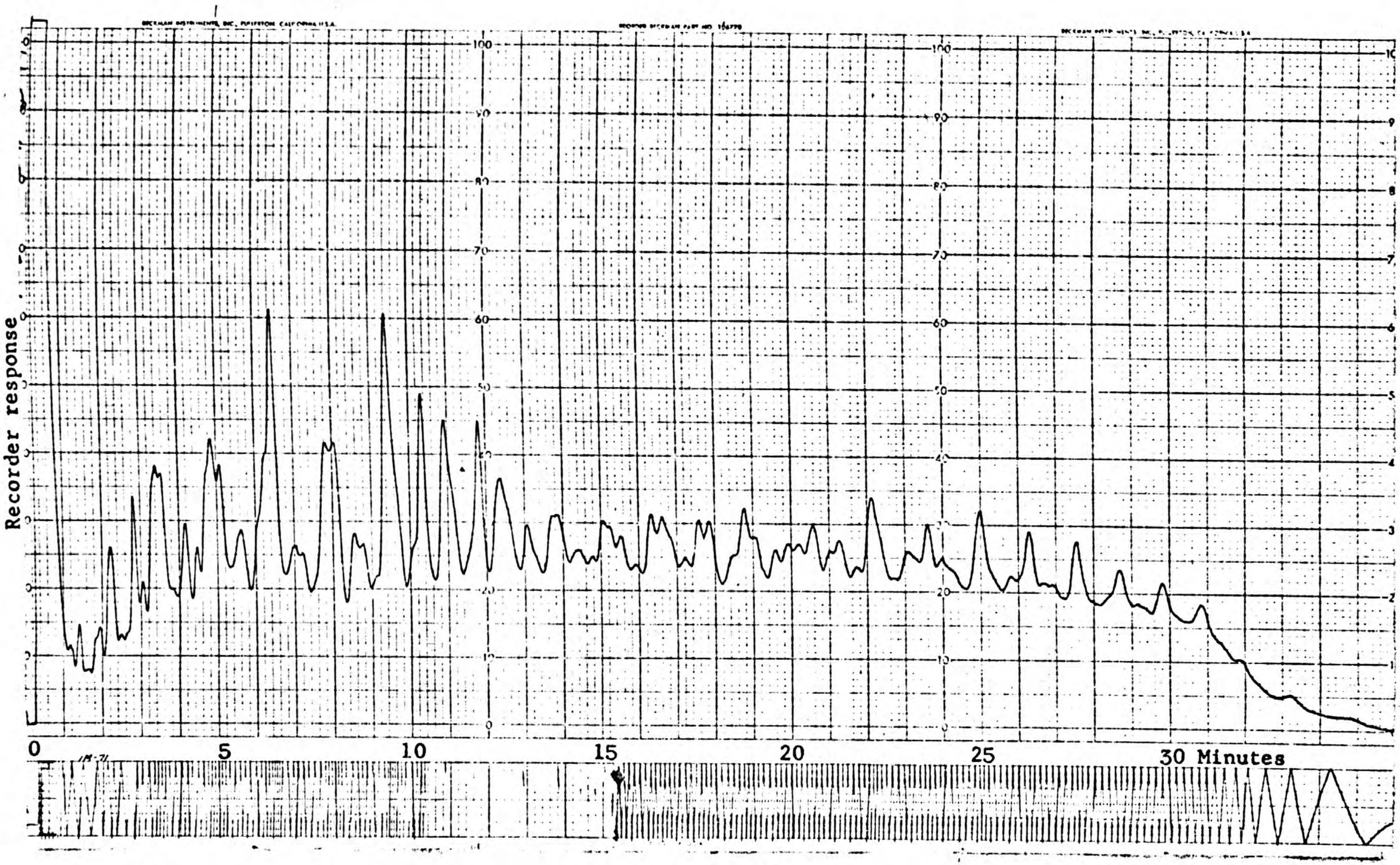

Figure 13. - Gas chromatogram of Papoose Cañon oil, branched-cyclic saturated hydrocarbon fraction

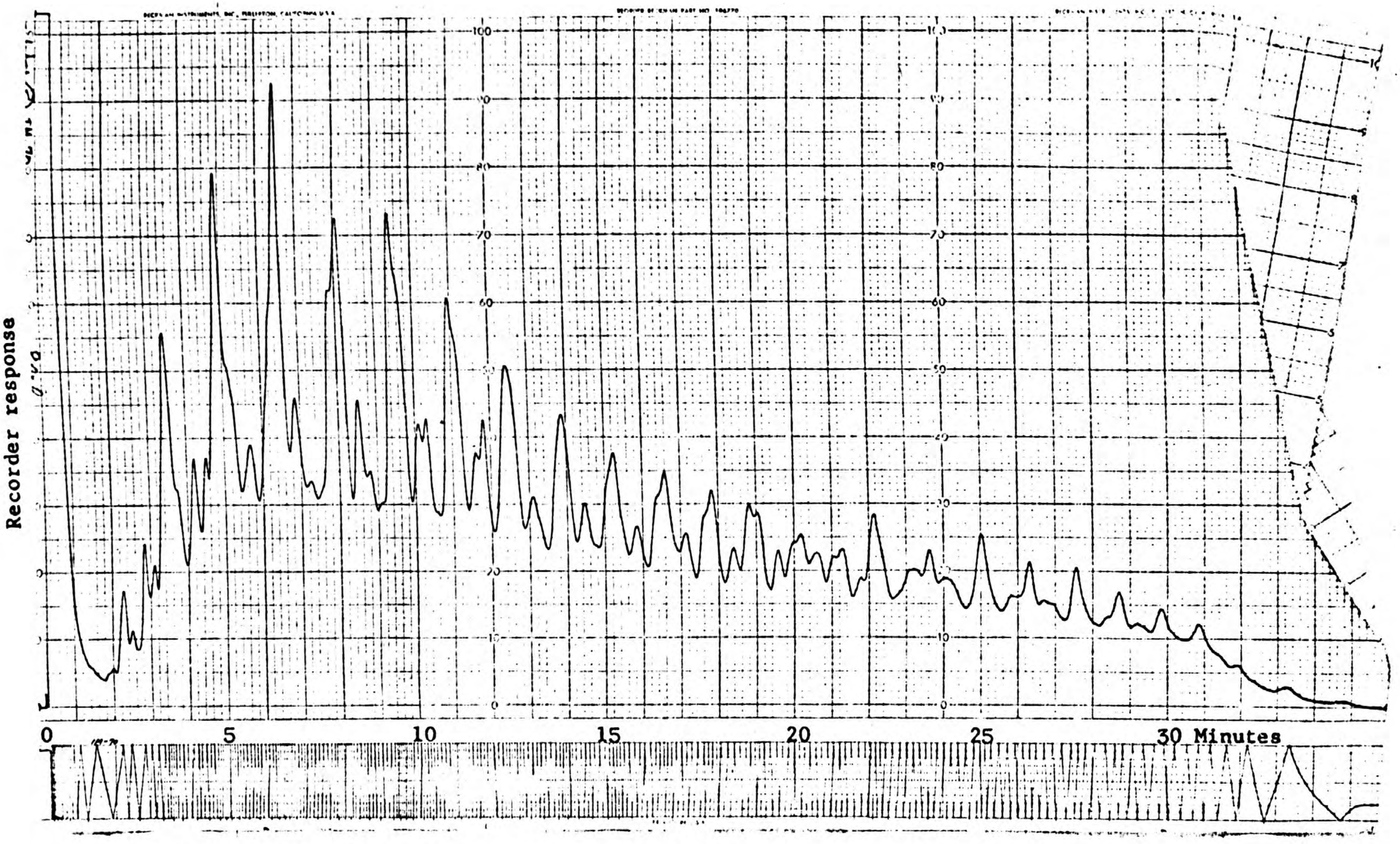

Figure 14. - Gas chromatogram of Lisbon oil, branched-cyclic saturated hydrocarbon fraction

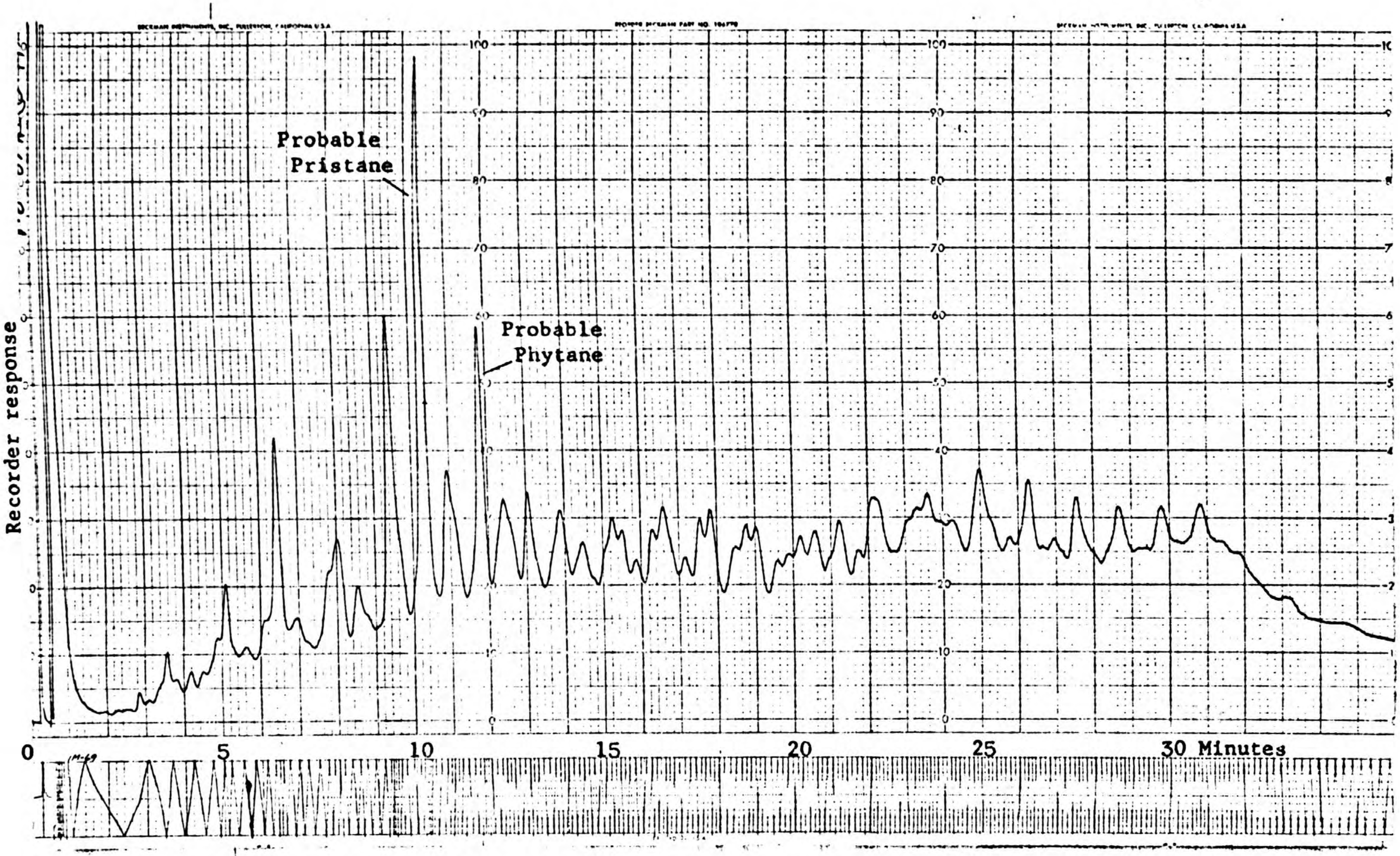

Figure 15. - Gas chromatogram of Sierra oil, branched-cyclic saturated hydrocarbon fraction

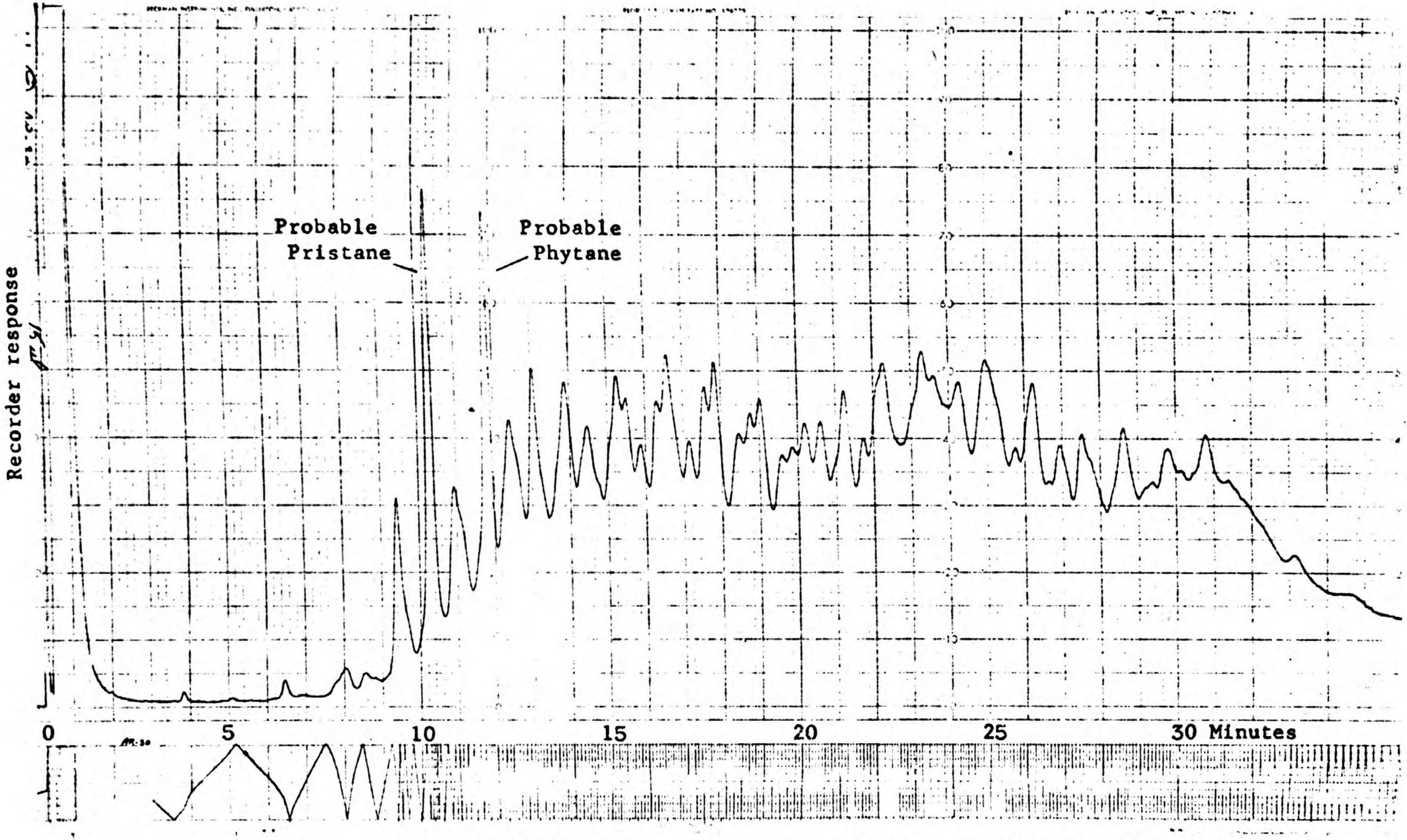

Figure 16. -Gas chromatogram of Idarado mine sample no. 8, branched-cyclic saturated hydrocarbon fraction

The chromatograms of the saturated hydrocarbon fractions of the extracts of the mine samples (figs. 7-11) indicate a relationship between the composition of the extracts and the distance of the respective sample sites from the possible source sediments. The n-alkane compounds are present in the greatest amount in the extract from mine sample no. 8, (fig. 11), which is from the sample site nearest the possible source sediments (fig. 2); lesser amounts of n-alkanes are in the extracts from the other mine samples (figs. 7-10), which were collected at points farther from the possible source sediments, in the plane of the Montana-Argentine vein (fig. 2).

Many researchers have noted the "chromatographic" effect of sediments on crude oils during oil migration (for example: Bonham, 1956; Hodgson and others,1957; Nagy, 1960; Thompson, 1962; Colombo and Sironi, 1961; Baker, 1962; McAuliffe, 1963; and Silverman, 1965). During its migration through sediments, petroleum is more likely to become enriched in saturated hydrocarbons, through the selective retention of the more polar aromatic hydrocarbon and asphaltic compounds. The effect observed in the extracts from the Idarado mine may be different, however. The gas-liquid chromatographic evidence indicates a depletion of n-alkane compounds, and a possible depletion of all saturated hydrocarbons, with increased distance of migration upward and from south to north through the volcanic rock. Three mechanisms might account for this observed change: the physical entrapment of certain molecules (analagous to the action of a molecular sieve) during the migration; the thermal degradation of part of the saturated hydrocarbons by the solidified, but still hot, volcanic rocks; and the aforementioned "chromatographic" separation, allowing the entire saturated fraction to migrate past the sample sites in the mine. Any such theory assumes, of course, that the oil materials from the different mine locations have a common origin.

Emission spectrographic and X-ray fluorescence data

The emission spectrographic data (table 6) show that many elements

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Table 6.--NEAR HERE

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are present in the ash of the oil extracted from the mine rock, and in the ash of the Sierra crude oil, chosen for comparison with the mine samples because of its similarity in the carbon and sulfur isotope and in the gas-liquid chromatographic studies. Only four of 34 metals in the determination (Au, Sb, W, and Nb) were not detected in any ash sample from the mine. Several metals—Zn, Mn, Pb, Sr, Fe, Mg, and Ca—were found in high concentration, over 1,000 ppm, in most ash samples from the mine.

A comparison of the composition of the ash of extracts of mine samples and the Sierra crude oil reveals that nine metals (Ti, Zn, Mn, La, Pb, Y, Mo, Be, and Sc) are present in at least three mine-sample extracts in greater concentration than in the crude-oil ash, with three metals (Zn, Pb, and Y) at least five times as concentrated in three or more of the ashes of mine-sample extracts than in the crude oil ash. On the other hand, the Sierra oil ash sample has 11 metals (V, Zr, Ni, Co, As, Cr, Ba, Sr, Fe, Mg, and Ca) in greater concentration than in three or more mine-sample extracts, with 10 of these metals (excluding Mg) at least five times more concentrated in the Sierra oil ash than in three or more of the extracts. It is interesting to note that Zn and Pb, two of the metals produced from the mine, are more concentrated in the ashes of extracts of the mine rock than in the crude-oil ash, and that several metals frequently associated with crude oil, such as

V, Ni, and Fe (Erickson and others, 1954; Bell, 1960; Dwiggins and others, 1969) are more concentrated in the Sierra crude-oil ash than in the ashes of mine-sample extracts. It has been suggested (S. R. Silverman and J. M. Sugihara, oral commun., 1969) that most of the metals found in crude oil, or in the ash of crude oil, are minute particles of the reservoir rock, which are not separable from the oil by centrifugation or filtration. The differences in metal content between the extracts of mine samples and the Sierra crude oil may therefore be attributed to the differences in composition of their respective reservoir rocks. In fact, the suite of metals is generally the same for the extracts and the crude oil. In most cases, if a particular metal is highly concentrated in one, it is also concentrated somewhat in the other. This may be taken as a slight indication that the Sierra crude oil and the extracts of mine samples were of a common origin.

Table 6.--Semiquantitative emission spectrographic data 1/

Element	Ti	Zn	Mn	V	La	Ni	Cd	Zr	Mo	Sn	Co	W	Fe,%	Mg,%	Ca,%
Idarado mine															
No. 2	70	10,000	5,000	30	100	100	$<\overline{100}$	200	5	$<\overline{10}$	$<\overline{20}$	$<\overline{50}$	1	0.2	5
No. 3	150	>10,000	3,000	70	>1,000	150	150	20	5	$<\overline{10}$	$<\overline{20}$	$<\overline{50}$	5	.1	7
No. 4	200	700	3,000	10	$<\overline{100}$	30	$<\overline{100}$	$<\overline{20}$	$<\overline{2}$	$<\overline{10}$	$<\overline{20}$	$<\overline{50}$	.1	.07	2
No. 5	70	7,000	1,500	10	$<\overline{100}$	50	150	$<\overline{20}$	<2	$<\overline{10}$	$<\overline{20}$	$<\overline{50}$	.05	.05	2
No. 6	150	500	>5,000	70	1,000	100	$<\overline{100}$	$<\overline{20}$	15	$<\overline{10}$	$<\overline{20}$	$<\overline{50}$	5	.2	5
No. 8	3,000	>10,000	5,000	1,500	$<\overline{100}$	>5,000	300	70	7	30	200	$<\overline{50}$	.7	.5	1.5
Sierra crude oil	100	2,000	2,000	150	$<\overline{100}$	500	100	50	$<\overline{2}$	$<\overline{10}$	50	$<\overline{50}$	>20	.3	>20

Element	Cu	Pb	Sr	Y	Ba	B	As	Ag	Be	Bi	Sb	Nb	Au	Sc	Cr
Idarado mine															
No. 2	700	>20,000	>5,000	150	200	150	$<\overline{100}$	20	10	$<\overline{20}$	$<\overline{50}$	$<\overline{10}$	$<\overline{5}$	<20	5
No. 3	1,500	>20,000	>5,000	>200	200	200	$<\overline{100}$	100	10	20	$<\overline{50}$	$<\overline{10}$	$<\overline{5}$	100	20
No. 4	150	2,000	700	$<\overline{50}$	200	1,000	$<\overline{100}$	<.5	2	$<\overline{20}$	$<\overline{50}$	$<\overline{10}$	$<\overline{5}$	$<\overline{20}$	$<\overline{5}$
No. 5	100	>20,000	700	>200	$<\overline{5}$	20	$<\overline{100}$	7	.7	<20	$<\overline{50}$	$<\overline{10}$	$<\overline{5}$	$<\overline{20}$	$<\overline{5}$
No. 6	150	7,000	2,000	>200	150	200	$<\overline{100}$	20	15	$<\overline{20}$	$<\overline{50}$	$<\overline{10}$	$<\overline{5}$	<20	5
No. 8	1,500	3,000	700	$<\overline{50}$	1,000	>2,000	$<\overline{100}$	30	3	<20	$<\overline{50}$	$<\overline{10}$	$<\overline{5}$	$<\overline{20}$	300
Sierra crude oil	200	2,000	>5,000	50	>5,000	200	500	20	3	$<\overline{20}$	$<\overline{50}$	$<\overline{10}$	$<\overline{5}$	$<\overline{20}$	100

1/ Analyst: James N. Nishi, U.S. Geological Survey. All results are parts per million (ppm) of metal in the ash, except where otherwise noted. Symbols are defined: < --less than; > --greater than; $<\overline{50}$ -not detected at 50 ppm, the lower limit of detection; <20-- present in concentration less than 20 ppm, the minimum standard.

Of perhaps greater interest is the comparison among the mine samples. One might expect the extracts from mine samples 2, 3, 4, 5, and 6 to have a different ash composition than the extract no. 8, because of the greater distance of migration through the volcanic rocks, or the longer contact time with the volcanic rocks. The ash of/extract no. 8 has a higher concentration than at least three ash samples of the other extracts for 15 metals (Ti, Zn, V, Zr, Ni, Cu, Cd, B, Mo, Sn, Co, Ag, Cr, Ba, and Mg), including nine metals (Ti, V, Ni, Cu, B, Co, Cr, Ba, and Mg) which are at least five times as concentrated in the ash of extract no. 8 as in two or more other mine-extract ash samples. On the other hand, seven metals (La, Pb, Y, Be, Sr, Fe, and Ca) are generally more concentrated in the ash of the other mine-sample extracts than in the ash of extract no. 8 with five metals (La, Pb, Y, Sr, and Fe) at least five times as concentrated in two or more ash samples than in extract no. 8. Four of the five metals produced from the mine (excluding gold) are represented in this comparison, with zinc, copper, and silver slightly more concentrated in the ash of extract no. 8, and lead much more concentrated in the other extracts. Vanadium and nickel, found in metallo-porphyrin complexes in crude oils (Dwiggins and others, 1969; Eisma and Jurg, 1969), are present in high concentration in the ash of extract no. 8, but are much diminished in the other ash samples, indicating that such sensitive complexes may have been destroyed during migration in hot volcanic rocks.

The high concentrations of La, Pb, Y, Sr, and Fe in the ash of samples from stratigraphically higher positions than site no. 8 may indicate that the oil somehow selectively accumulated these elements during the migration through the volcanic rock. The fact that many metals are more concentrated in the ash of extract no. 8 than in the other ash samples indicates that the metals were present in the oil as it began its migration in the volcanic rocks, but were reduced and deposited in the volcanic rocks somewhere between site no. 8 and the seven stratigraphically higher sites. More likely, however, the ash analyses by emission spectrography reflect local variations in composition of the rocks in contact with the oil.

X-ray fluorescence data (table 7) indicate a good uniformity in the ratio of vanadium to nickel concentration in the ashes of extracts from the mine samples. Unfortunately, this ratio cannot be accurately calculated for the Sierra oil sample using the X-ray data, because of the low value for vanadium. However, an approximate value, ≥ 0.2, is close to the ratios for the ashes of mine samples. Using the emission spectrographic data, the ratio V/Ni is 0.3 for the Sierra crude oil, in good agreement with the ratios obtained with the X-ray data for the ashes of extracts of the mine samples. The agreement between the X-ray data and the comparable emission spectrographic data is poor, probably due to differences in the techniques of sample preparation prior to analysis.

Table 7.--X-ray fluorescence data

[Analyst: J. S. Wahlberg, U.S. Geological Survey. ---, no determination]

Sample	Analysis of ash				
	Ash (percent)	Vanadium (ppm)	Fe_2O_3 (ppm)	Nickel (ppm)	V/Ni
Idarado Mine					
No. 2-----------	0.103	1.3	230	4	0.3
No. 3-----------	---	2.3	920	7	.3
No. 4-----------	.0634	.7	110	3	.2
No. 5-----------	---	1.0	160	4	.2
No. 8-----------	.00237*	2.1	17	9	.2
Sierra------------	.00188*	<.5	410	2	<.2
Redistilled benzene---------	.000575	---	---	---	---

* Average of two determinations.

Conclusions

The oil extracted from vein rocks of the Idarado mine is a dark viscous oil, with concentrations of saturated and aromatic hydrocarbons averaging 34.8 and 47.9 percent, respectively. Gas-liquid chromatographic data show a marked decline in n-alkane content of the extracts, from 60 to less than 5 percent, with increasing distance of the sample sites from the possible source sediments beneath the volcanic rocks of the mine. Silica-gel chromatographic data suggest this decline parallels a decline in the percentage of all saturated hydrocarbons with increasing distance from the possible source sediments.

Emission spectrographic data similarily indicate a definite difference in the composition of the several oil samples extracted from mine rocks. The concentrations of five metals (Pb, Sr, Fe, La, and Y) increase markedly, and the concentrations of nine other metals (Ti, V, Ni, Cu, B, Co, Cr, Ba, and Mg) decrease markedly with the increasing distance of the sample sites from the possible source sediments. Possible reasons for these changes in composition include: (1) the reduction and removal of certain metals, and the modification or removal of certain organic compounds by hot volcanic rocks, (2) the dissolving and transporting of certain metals by the oil, and the precipitating and filtering out of other metals from the oil, and (3) the change in composition of volcanic rock from one site to another.

The narrow ranges of values for the carbon and sulfur isotopic data indicate a common source for the oil from different sites in the Idarado mine. Only one of four crude oils analyzed, that from the Sierra field, compares well with the mine-oil samples for the isotopic data; $\delta^{13}C$ of -29.0 per mil compared with an average of -27.3 for the mine-oil samples, and $\delta^{34}S$ of -5.80 per mil, compared with an average of -5.44 for the mine-oil samples.

The gas-liquid chromatographic data also show a similarity between the Sierra oil and the oil extracted from the mine rocks. Two large peaks, probably representing the isoprenoid hydrocarbons pristane and phytane, are present in the chromatograms of branched- and cyclic-saturated hydrocarbon fractions of the oil from the Sierra field and from the mine rocks. These peaks are small or absent in corresponding chromatograms of the oils from the other three fields.

Thus of the four crudes tested, the crude oil from the Sierra Field, Montezuma, Colo., is most likely to be from the same source as the oil found in the Montana-Argentine vein of the Idarado mine, Ouray County, Colo., based on similarities in isotopic and gas-liquid chromatographic data. The mine oil most likely migrated during or after the most recent intrusive activity, in late Tertiary time, from a possible source in the Dakota Sandstone of Cretaceous age to the present locations in the Telluride Conglomerate and San Juan Formation of Tertiary age.

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