Oct. 3, 1967 C. D. McAULIFFE 3,345,137

GEOCHEMICAL METHOD OF PROSPECTING FOR PETROLEUM

Filed Sept. 24, 1965

4 Sheets-Sheet 1

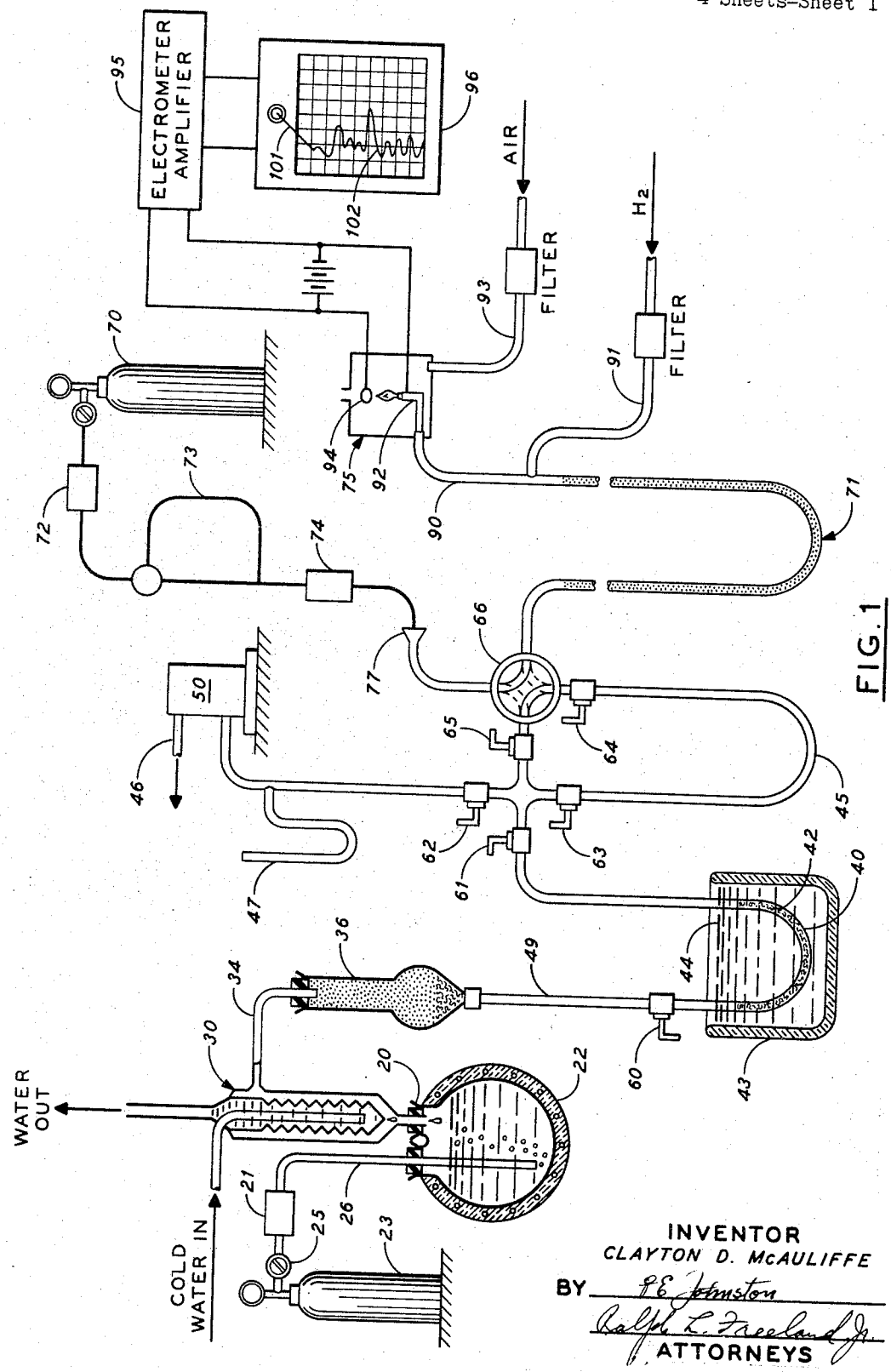


FIG. 1

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4 Sheets-Sheet 2

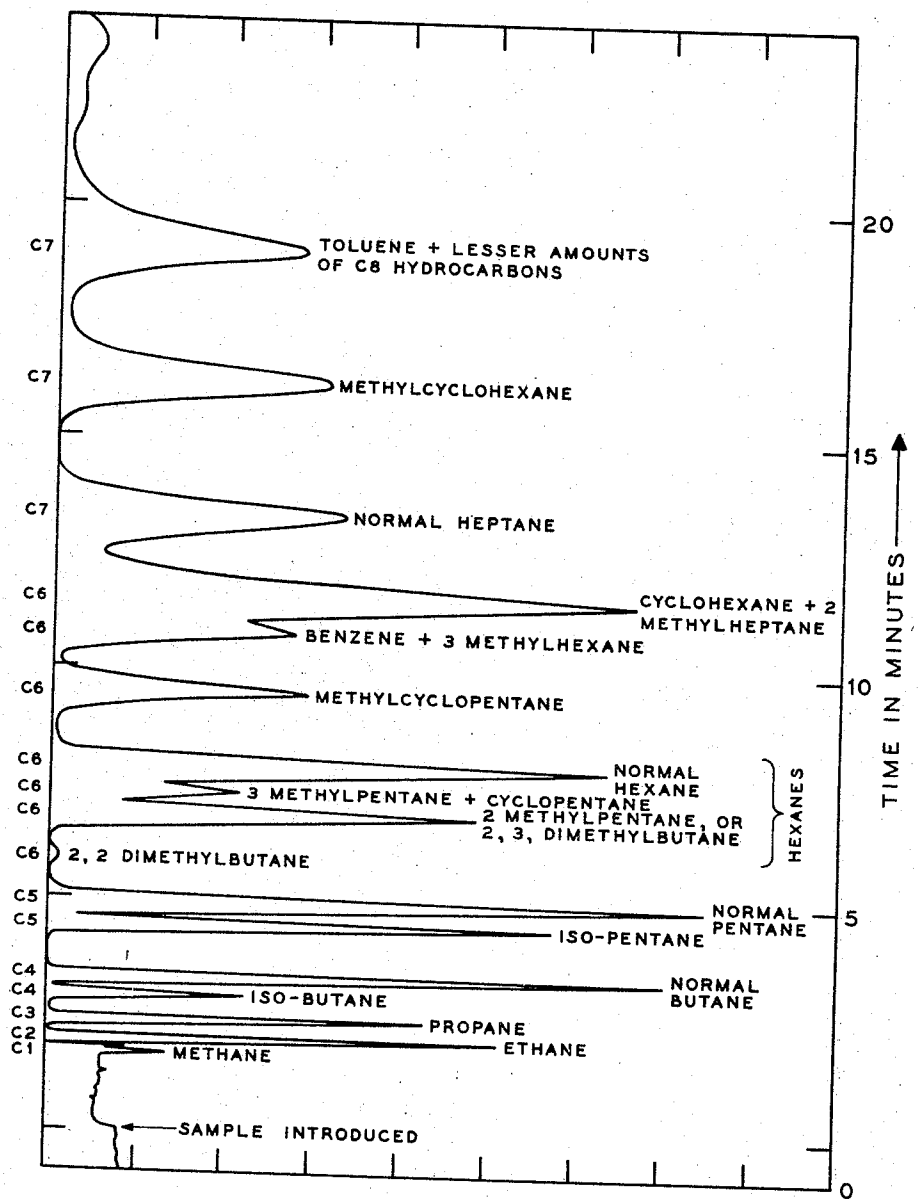


FIG. 2

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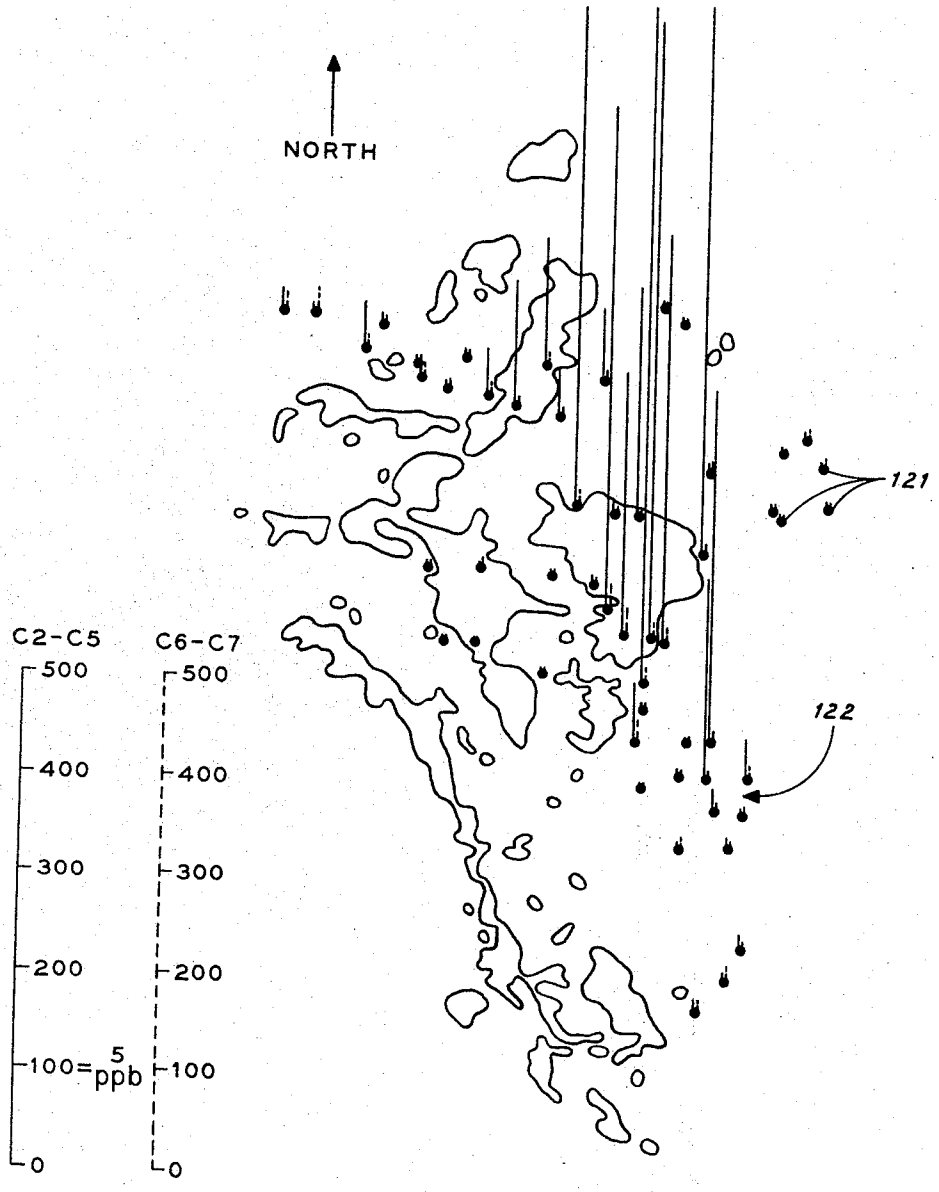


FIG.3

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GEOCHEMICAL METHOD OF PROSPECTING FOR PETROLEUM

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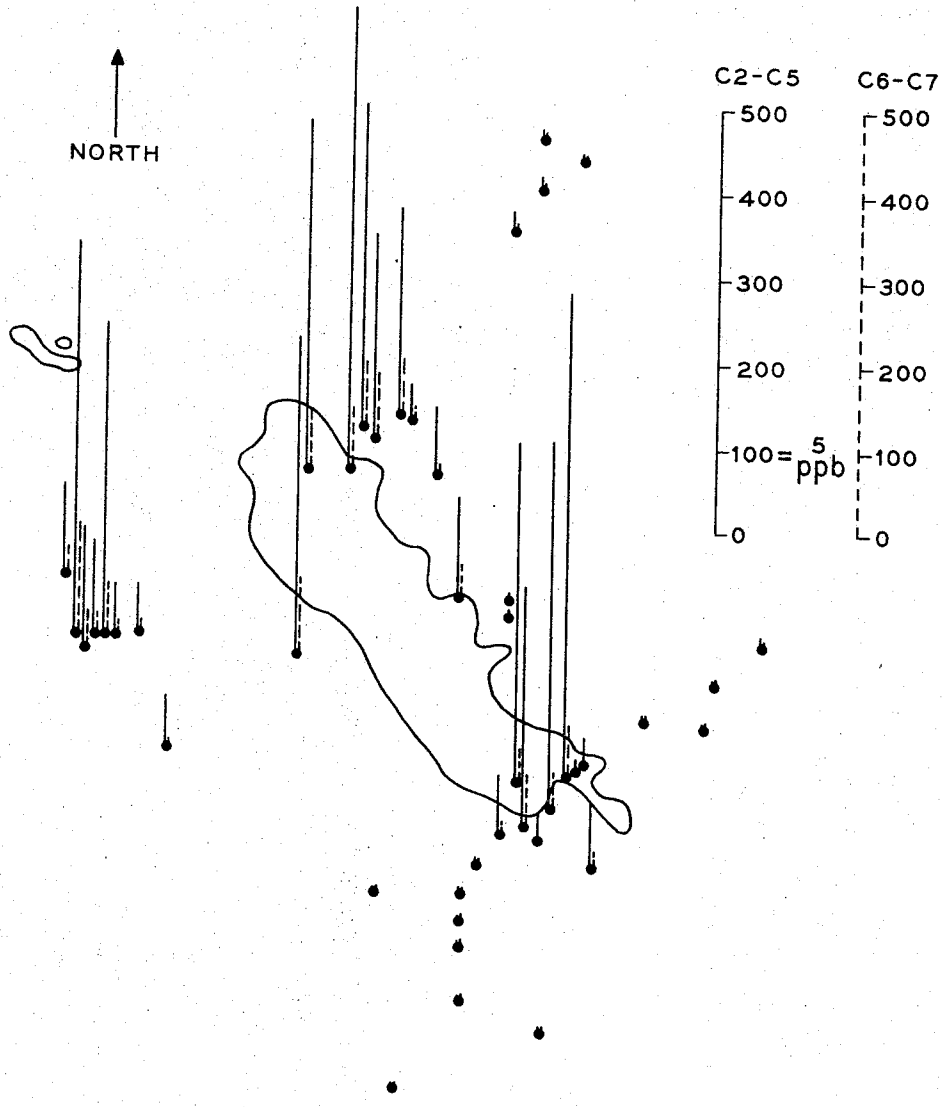


FIG. 4

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United States Patent Office

3,345,137

Patented Oct. 3, 1967

3,345,137

GEOCHEMICAL METHOD OF PROSPECTING FOR PETROLEUM

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Filed Sept. 24, 1965, Ser. No. 492,987
4 Claims. (Cl. 23—230)

This application is a continuation-in-part of application Ser. No. 174,172, filed Feb. 19, 1962, and now abandoned.

This invention relates to geochemical prospecting for petroleum, and more particularly this invention relates to a method of preserving the hydrocarbon content of samples collected from an area for analysis of said samples for a selected range of hydrocarbons including hydrocarbons having from two through seven carbon atoms, which selected hydrocarbons are indicative of petroleum accumulations in subterranean formations.

Searching for a direct indication of subsurface petroleum in its most basic form is looking at the earth's surface for visible indications of subsurface petroleum accumulations. The most obvious indication of subsurface petroleum is a surface oil seep. Less obvious but still visible direct indications of subsurface petroleum include gas seeps bubbling through a body of water. However, in addition to all the visible seeps of both gas and oil there are many surface and subsurface seeps that are not visible to even close visual inspection. Geochemical prospecting as a direct indication of petroleum developed on the basis that oil and gas contain water-soluble constituents and these constituents should be detectable by chemical methods in water or earth which comes in contact with the oil or gas. Many forms of geochemical exploration have been tried heretofore. However, for a variety of reasons, none of these methods have proved entirely satisfactory.

Generally, geochemical exploration for petroleum comprises collecting samples from an area which may be, for example, many square miles in size. Each sample is later analyzed to determine the hydrocarbon content of the sample. The results of this analysis are then correlated with the surface location where each sample was collected and the locations of high hydrocarbon-containing samples may be indications of the presence of subterranean petroleum accumulations.

It is one object of the present invention to provide a method of geochemical prospecting which includes collecting samples from near surface locations of an area of the earth, preserving any hydrocarbons contained in said sample, separating said hydrocarbons from said sample and quantitatively examining said hydrocarbons for the presence of selected fractions therein.

In the present invention geochemical prospecting as a method of finding petroleum comprises the steps including sampling and sample preservation, separating the hydrocarbons from the sample, analyzing the hydrocarbons for the presence of selected hydrocarbons containing from two through seven carbon atoms, and correlating the results of the analysis with the surface location from where each sample was collected to provide an indication of the presence of a petroleum deposit.

Briefly, the present invention provides for collecting samples from different locations of an area of the earth. The samples are preferably liquid samples. Water samples are obtainable, for example, from wells or other places where underground water is accessible. Suitable samples

can be collected from the fluid in seismic shot holes, for example. Since sampling is often conducted on barren terrain far removed from convenient transportation, it is desirable that the size of the sample be relatively small. However, the hydrocarbons in a sample may be as little as one part per billion or less. Therefore, the sample must be large enough to allow for analysis to determine the presence of minute quantities of hydrocarbons. The methods of this invention provide for satisfactorily determining the presence of selected hydrocarbons from samples of about one-half gallon of water or about one pint of drilling fluid. The samples are desirably collected in containers which will not contribute or removed hydrocarbons from the sample. Because the lightest hydrocarbons, that is, those containing from one to three or four carbon atoms, will readily escape from water, the container must be air-sealed and the dead air space in the container kept to a minimum. Some of the light hydrocarbons will be lost while filling the sample container with the sample; however, this is not serious since the loss will generally be proportionally the same for each sample and the method of the invention is concerned with relative differences in hydrocarbon content and not the absolute hydrocarbon content of any given sample.

It is an important feature of the present invention that the hydrocarbons in the sample be protected with a bactericide from the time the sample is collected. Certain types of bacteria found in water destroy hydrocarbons in a relatively short time. These bacteria are common in most ground water. In the past, many attempts at geochemical prospecting failed because of hydrocarbon destruction in the sample by bacteria. It has been found that the hydrocarbons in a sample will often be appreciably reduced in two or three days and substantially destroyed in seven to ten days from the time of collection. Since in field practice the delay between sampling collection and laboratory analysis often requires much longer periods, it is critical to the success of the method that the hydrocarbons contained in the samples be protected from destruction by bacteria. The method of the present invention provides for adding a bactericide to each sample to preserve any hydrocarbons contained therein.

The hydrocarbons contained in each sample are separated from the liquid. The separation is accomplished using a reflux condenser with a carrier gas sweep to produce a hydrocarbon carrying effluent. Carbon dioxide and water vapor are removed from the effluent. The hydrocarbons are separated from the effluent prior to analysis for selected hydrocarbons.

The method provides for analyzing the recovered hydrocarbons for hydrocarbon fractions containing from two through seven carbon atoms. This range, as discussed hereinafter, is especially desirable to distinguish a true anomaly from high hydrocarbon content of a sample caused by surface contamination. The present method provides for substantially complete separation and quantitative analysis of the hydrocarbons from ethane to toluene. In the preferred embodiment the analysis is accomplished by a gas-liquid partition chromatograph. Generally, a gas-liquid partition chromatograph comprises a column packed with solid particles covered with a nonvolatile liquid. The gaseous hydrocarbon mixture recovered from the sample is transported through the column by a chromatograph carrier gas, usually helium. The hydrocarbons travel through the column at varying rates depending on the amount of absorption of the various fractions by the packed column. The lighter (C_2–C_3, etc.) hydrocarbon fractions spend relatively less time in the column because

they tend to be less absorbed than the heavier fractions. As the individual hydrocarbons emerge from the column, their concentrations are measured quantitatively. A hydrogen flame ionization detector is one means of quantitatively measuring the hydrocarbons. The detector signal is amplified and recorded with a strip chart potentiometer. From this graph the concentration of each fraction is determined for each sample.

The concentrations of the hydrocarbons as represented on the chart may be obtained by many methods. One method of obtaining the concentration of the hydrocarbons is integrating the area under each individual peak with a planimeter. In accord with the present invention the concentration of the hydrocarbons containing from two through five carbon atoms are totaled and the concentration of hydrocarbons containing six and seven carbon atoms are totaled. Thus a figure representative of the concentration of C_2–C_5 hydrocarbons is obtained and a a figure representative of the C_6–C_7 hydrocarbons is obtained.

The concentrations of C_2–C_5 and C_6–C_7 fractions of each sample are transferred graphically to locations on a map corresponding to the location of collection of the sample. The areas of likely petroleum accumulations are determined from this map by one skilled in the art.

Further advantages and objects of the present invention will become apparent from the following detailed description read in view of the accompanying drawings which are made a part of this specification.

FIG. 1 is a diagrammatic illustration of a preferred embodiment of apparatus useful in practicing the method of the present invention.

FIG. 2 is a chart representative of hydrocarbons contained in a sample.

FIG. 3 is a map showing the boundaries of known underground petroleum accumulations and the hydrocarbon content of samples collected from the area.

FIG. 4 is a map showing the boundaries of known underground petroleum accumulations and the hydrocarbon content of samples collected from the area.

FIG. 4 is a map showing the boundaries of known underground petroleum accumulations and the hydrocarbon content of the samples collected from the area.

In accordance with the present invention, samples are taken from locations of the area being prospected. Sample density, i.e., the number of samples taken per unit area, depends on a number of facts including the type and extent of the survey, the accessibility of sampling locations and other factors. The light hydrocarbon content of the water sample must be representative of the liquid being sampled. Therefore the samples should be collected from a place where the liquid has had minimum contact with the atmosphere. The samples are usually taken from locations relatively near the earth's surface. It is often convenient to take samples from water wells located in an area.

The sample containers are desirably constructed of material inert with respect to the sample. Glass bottles having Teflon-lined caps are an example of a suitable sample container. Sample size may vary. However, when practicing the method of the present invention, it is preferred to collect one-half gallon samples of water or one-pint samples of drilling fluid to provide adequate hydrocarbons for separation and analysis. The sample containers are gas-sealed and are shipped and stored upside down to prevent gas leakage.

As indicated above, one of the most serious problems with geochemical prospecting has heretofore been bacterial destruction of the hydrocarbons in the samples before analysis. In fact, laboratory experiments have shown substantial hydrocarbon deterioration in two to three days and complete destruction of the hydrocarbon content of a water sample in less than a week caused by bacteria. The present invention provides for preserving the hydrocarbon content of the samples from destructive bacteria by providing a bactericide to control the bacteria. The bactericide used in the method must not interfere with the analysis for hydrocarbons. When a bactericide is used as taught herein a sample may be stored several months without appreciable loss of the hydrocarbons contained in the sample.

The bactericide is added to the sample when the sample is first collected. A desirable means of providing protection from bacteria is to add the bactericide to the collection bottles prior to collecting the sample. In this manner the bactericide is mixed with the sample when the sample is collected.

Compounds found useful as bactericides include simple mercury salts, methyl blue, acriflavine, and combinations of these compounds. Simple mercury salts, especially mercuric chloride ($HgCl_2$), have been used as disinfectants. It has been demonstrated that the antibacterial action of mercury can best be explained on the basis that it interferes with some essential cellular metabolite, such as certain R—SH compounds. Mercury combines with —SH groups in the bacterial cell to form a chemical complex and thus deprives the cell of —SH groups, which are essential for its metabolism. Within limits the action of mercury is merely the inactivation of the —SH group without other demonstrable injury to the cell. Thus, mercuric chloride, by this mode of action, is a general bactericide effective against all bacteria. As shown below it is very effective in preventing bacterial destruction of hydrocarbons in water. The bactericides may be prepared for use in a variety of ways. Below are examples of solutions of the bactericides which have prevented destruction of hydrocarbons in water by bacteria.

An example of a bactericide useful in the invention is a water solution of mercuric chloride. A solution containing about 40 grams mercuric chloride per liter has given excellent results when about 5 ml. of the 40 grams/liter solution is added to a one-gallon water sample containing hydrocarbons. The 5 ml. of 40 grams mercuric chloride per liter/gallon of hydrocarbon-containing sample dose is mixed with the sample when the sample is initially collected. In this manner, the hydrocarbon content of the sample is protected from bacteria.

Another example of a suitable bactericide for preserving the hydrocarbon content of a sample is methylene blue. A water solution of methylene blue containing about one gram methylene blue per liter has been found to give adequate protection from bacteria when about 5 ml. of this solution is added per gallon of water sample collected.

Another example of a bactericide useful in the method of the invention is acriflavine (neutral). A dose of about .2 gram of acriflavine (neutral) per gallon of water sample collected has given good results. The dose should be added to the sample in the field when the sample is collected.

Another bactericide effective in preventing destruction of hydrocarbons by bacteria in water samples is a mixture of mercuric chloride and methylene blue. A ratio of 400 mgs. of mercuric chloride to 5 mgs. of methylene blue per gallon of water sample is useful in protecting any hydrocarbons contained therein from bacteria.

In experiments run to test the effectiveness of bactericides in preventing destruction of hydrocarbons by bacteria, water containing dissolved hydrocarbons was prepared by bubbling natural gas through 5 gallons of water for about 4 minutes. After thorough mixing, an aliquot of the water was sealed in ½- or 1-gallon bottles. Some of the bottles were treated with a bactericide while others were not. The type and dose of the bactericide used is indicated in the summarization. After selected time intervals, the bottles were opened and the water analyzed for their hydrocarbon content by the method herein described. The results of these experiments are summarized below. To prevent an excessively large summarization, only the concentrations of representative hydrocarbons of all those analyzed for containing from two through seven carbon atoms have been included in the summarization.

EFFECTIVENESS OF SELECTED BACTERICIDES IN PREVENTING DESTRUCTION OF HYDROCARBONS[1] DISSOLVED IN WATER

	Elapsed time in days	Hydrocarbon concentration (relative units)					
		Ethane	Propane	N-Butane	N-Penatne	N-Hexane	Methylcyclo-hexane
[Mercuric chloride treatment (400 mgs. per gallon of water)]							
Experiment 1:							
Untreated water	0	52.3	18.1	6.3	1.5	.54	1.05
	7	4.2	5.9	3.2	.5	.15	.20
	14	[2]	[2]	[2]	[2]	[2]	[2]
Treated water	0	[3]	[3]	[3]	[3]	[3]	[3]
	7	55.6	18.6	6.0	1.6	.54	1.11
	7	48.9	18.7	6.5	1.5	.53	.93
	7	31.5	13.5	4.4	1.2	.34	.72
	7	46.2	20.1	6.6	1.7	.47	1.08
Experiment 2:							
Untreated water	0	115	68.2	22.4	3.80	.71	1.42
	14	[2]	[2]	[2]	[2]	[1]	[2]
Treated water	0	[3]	[3]	[3]	[3]	[3]	[3]
	11	117	67.8	21.9	3.51	.72	1.51
	20	114	69.0	23.0	3.87	.68	1.31
	28	94	57.6	18.9	3.21	.56	.99
	38	140	86.1	28.6	4.56	.75	1.40
[Mercuric chloride (400 mgs./gal. H_2O)+Methylene blue (5 mgs./gal. H_2O)]							
Untreated water	0	30.6	14.7	4.45	1.15	.37	.42
	7	3.4	6.7	3.01	.48	.10	.24
	13		.03				
Treated water	7	26.1	13.1	4.20	.99	.37	.35
	13	35.1	14.9	4.86	1.23	.36	.53
[Acriflavine (neutral)—200 mgs./gal. H_2O)]							
Untreated water	0	112	70.2	24.1	4.20	1.86	1.63
	17	[2]	[2]	[2]	[3]	[2]	[2]
Treated water	12	106	61.8	22.6	3.96	1.85	1.67
	20	117	78.9	25.7	4.35	1.82	1.64

[1] To prevent excessively large tables, the concentration of only representative hydrocarbon of those analyzed is shown.
[2] No detectable hydrocarbon.
[3] Same as for untreated water.

As is evident from the above summarized experiments, the addition of a bactericide to a sample when it is collected is critical to the success of a method of geochemical prospecting. It has been found that many geochemical surveys heretofore which depended on analysis of water or soil samples for relatively small hydrocarbon content have been unsuccessful due primarily to the extent that the hydrocarbons contained in the samples were destroyed by bacteria prior to analysis. Utilizing the method of this invention and the bactericides as provided herein, good results are obtainable.

Referring now specifically to FIG. 1, a preferred embodiment of apparatus with which the hydrocarbons contained in a water sample may be separated from the sample and quantitatively analyzed is shown. As there shown a flask **20** provided with a heating mantle **22** is connected by tubing **26** to a gas cylinder **23**. The system is flushed with gas, which might be, for example, nitrogen, from cylinder **23** to displace air which might contain hydrocarbon constituents. The sample is then placed in flask **20**, preferably by nitrogen gas displacement from the collection bottle. The temperature in flask **20** is raised to the boiling point of the liquid contained therein. A carrier gas, for example, nitrogen, from cylinder **23** is flowed through a silica-gel, activated carbon filter **21** into flask **20** by means of conduit **26** through regulator **25** and bubbled through the sample. The sample is therefore subjected to evaporative conditions in the presence of the carrier gas. The filter **21** is used to remove possible traces of hydrocarbons from the nitrogen. Other gases, for example helium or hydrogen, which may be used in place of nitrogen in the present invention should also be flowed through appropriate filters similar to filter **21** to remove trace hydrocarbons. The sample is subjected to evaporative conditions in the presence of carrier gas and therefore C_1 and C_7 hydrocarbons contained in the sample are volatilized and carried out of the sample in the effluent to a reflux condenser **30**. Water vapor is condensed in condenser **30** and falls back into flask **20**. The effluent which then flows out of condenser **30** through conduit **34** is made up primarily of carrier gas, gaseous hydrocarbons, and traces of water vapor, CO_2, and other volatile gases, for example oxygen, which may be present in the sample. The effluent enters drying tube **36** which is filled with a material such as ascarite which removes water vapor and CO_2 from the effluent.

Prior to analysis for individual hydrocarbons, the hydrocarbons are separated from the carrier gas. The preferred means of accomplishing the separation is described below. From drying tube **36** the effluent which now contains primarily carrier gas, oxygen, and hydrocarbons is flowed through conduit **49** to U-tube **40** which may be glass and which is packed with glass wool **42**. Conduit **49** has a restricted opening which regulates the gas flow through the system to 100–200 ml. per minute.

A preferred method of separating the hydrocarbons from the carrier gas is cooling the hydrocarbon-carrier gas effluent to a temperature at which the hydrocarbons become liquid or solid while the carrier gas and oxygen remain as gases and can be drawn from the relatively immobile hydrocarbons. One means of accomplishing this is to submerge U-tube **40** in a container **43** of liquid nitrogen **44**. The temperature in U-tube **40** is desirably below about —190° C. The temperature in container **43** is about —196° C. Since the gaseous hydrocarbons of interest freeze or liquefy at temperatures above —196° C., they are solidified or liquefied in U-tube **40**, and the carrier gas, in this case nitrogen, passes through U-tube **40** to be exhausted from the system at vent **46**. A vacuum is exerted on the system by means of a vacuum pump **50** to prevent oxygen gas from liquefying in U-tube **40**. The capillary **49** is of such size that the gas flow is 100–200 ml. per minute, and the vacuum measured at manometer **47** located between tube **49** and the vacuum pump **50** is 27–29 inches of mercury, a pressure adequate to prevent oxygen from liquefying in U-tube **40**. Under these conditions most of the methane (C_1) is lost. Ethane (C_2) and higher hydrocarbons however, are completely held in U-tube **40**.

Carrier gas is flowed through the sample in flask **20**

until substantially all the hydrocarbons having carbon numbers from one through seven, are removed from the liquid. Generally, substantially all these hydrocarbons will be removed from the sample in flask **20** in about 10 to 15 minutes after the sample reaches its boiling temperature.

After substantially all the hydrocarbons have been liquefied or solidified in U-tube **40** as described above, valve **60** is closed to stop the flow of carrier gas through U-tube **40**. The vacuum on U-tube **40** is increased to less than 1 mm. of mercury with valve **61**, valve **62**, and valve **63** open and valve **64** and valve **65** closed. Valve **66**, which is a two-way valve and represented schematically in FIG. 1, is adjusted to a position to close the loop formed by the tubing connecting valve **63**, valve **64**, and valve **65**. When two-way valve **66** is in this position, gas from cylinder **70** passes directly to chromatographic column **71** through pressure regulator **72**, flow regulator **73**, flow meter **74**, tubing **77**, and valve **66**. By maintaining U-tube **40** under vacuum, the methane content of the hydrocarbons frozen therein is almost completely lost. However, ethane and higher hydrocarbons are retained in U-tube **40**. Valve **62** is now closed. The liquid nitrogen container **43** is removed from U-tube **40** and placed in similar position to submerge U-tube **45**. Valve **61** and valve **63** are open, and the hydrocarbons of interest gasify as the temperature in U-tube **40** is increased by placing boiling water around U-tube **40**. The hydrocarbons are moved from U-tube **40** to U-tube **45** where they are again solidified or liquefied by the low temperature therein. After a determinable time, approximately 10 minutes, valve **61** and valve **63** are closed, and the hydrocarbons are trapped in U-tube **45** ready to be flowed into the detecting apparatus for analysis of the individual hydrocarbon fractions.

To flow the hydrocarbons from U-tube **45** into the detection apparatus, valve **63**, valve **64** and valve **65** are opened and valve **66** turned to permit the gas chromatograph carrier gas contained in cylinder **70** to flow through U-tube **45**. The hydrocarbons contained in U-tube **45** are flash volatilized by removing liquid nitrogen from around U-tube **45** and replacing it immedately with boiling water. The volatilized hydrocarbons are swept by the carrier gas into the chomatographic column **71**. The gas chromatograph carrier gas from cylinder **70** may be, for example, helium.

The detection apparatus for determining the concentration of the individual hydrocarbons is preferably a gas chromatograph. The gas chromatograph consists of two interrelated but essentially independent systems: a carrier-gas and sample system and an electrical sensing system. It is convenient to first describe each of these systems independently and then describe the consequences of flowing the hydrocarbons from the sample into the chromatograph assembly.

The gas system begins with a cylinder of compressed gas **70**. This gas is usually helium, nitrogen or air, but may be any gas appropriately chosen to be used with the detector system. The pressure in cylinder **70** is reduced to an appropriate working pressure by regulator **72**. The flow rate of the carrier gas is then controlled by the flow regulator **73**, and the rate of flow measured by flow meter **74**. The constant flow of carrier gas leaving regulator **73** passes sequentially through the following parts of the chromatograph: flow meter **74**, two-way valve **66**, directly to column **71** or (depending on the adjustment of valve **66**) through valve **65**, valve **63**, U-tube **45**, and valve **64** to chromatographic column **71**. The above-mentioned valves and associated tubing are maintained at 100° C. when the hydrocarbons are being flowed therethrough to prevent condensation of hydrocarbons.

The sensing elements may take many forms. In gas chromatographs utilizing helium or nitrogen as a carrier gas, the sensing elements are characteristically thermal-conductivity detectors. When the carrier gas is air, the sensing elements may be a catalytic combustion detector. A hydrogen flame ionization detector is illustrated in FIG. 1 and will be described. The hydrogen flame ionization principle provides a very sensitive method for measuring hydrocarbons. The detector does not measure inorganic compounds and fixed gases. Therefore it is a preferred apparatus for use in measuring hydrocarbons in the present invention. The hydrogen flame detector, represented generally by **75**, ionizes the sample by combustion in flame. The helium effluent carrying the individual hydrocarbons which have been separated in chromatographic column **71** is mixed with hydrogen gas from conduit **91** in conduit **90** and flamed in burner **92**. The mixture is burned in air entering from conduit **93**, and the resulting ions are collected by a small electrode **94** above the flame. Detection is based on the measurement of the ion current and is proportional to the number of carbon atoms present in the flame. The ion current is amplified by amplifier **95**, and the amplifier output drives a strip chart recording potentiometer **96**.

In operation the vaporized hydrocarbons are carried from U-tube **45** in the helium stream of the gas chromatograph into column **71**. In column **71** the various components of this hydrocarbon sample interact with the stationary liquid constituting the column packing of column **71**. The separation of the hydrocarbon in the sample is brought about by interaction with the stationary liquid packing in column **71** according to the principles well known in gas chromatography art. A preferred liquid stationary phase for column **71** is a silicone gum-rubber such as General Electric SE–30. The effluent from column **71** then consists of carrier gas intermittently contaminated with a single separated hydrocarbon of the sample which was placed in the apparatus. As each of these hydrocarbons pass through detector **75**, it brings about a production of ions in the oxygen-hydrogen flame of the detector, resulting in an ion current described above. The ion current from the detector is fed into amplifier **95** and strip chart potentiometer **96** where a pen **101** traces a curve **102**. The amplitudes of individual excursions in the curve correspond to the amount of various hydrocarbons present in the original sample. If the chart of potentiometer **96** is moving in synchronism with the flow of carrier gas in the apparatus, then the position of each peak on the chart can be correlated with the specific hydrocarbon causing the peak according to the principles well known in the art. The concentration of the individual hydrocarbons is determined by measuring the area under the curve by any of several well-known methods.

Although the above described method of hydrocarbon analysis is preferred, other analytical methods can be used. For example, the separated hydrocarbons held in U-tube **45** may be introduced into an analytical mass spectrometer where the individual hydrocarbons can thereby be determined. The mass spectrometer technique permits an alternate method of analysis of C_2–C_7 hydrocarbons to the chromatographic separation and hydrogen flame ionization detection.

FIG. 2 illustrates a chart obtained from a strip chart potentiometer such as potentiometer **96** of FIG. 1 by the method of the present invention. As shown in FIG. 2 the hydrocarbons containing from two through seven carbon atoms have individual peaks. The concentration of the individual hydrocarbons is calculated from the chart which is a continuous recording of the hydrocarbons as they emerge from the chromatographic column. The exact concentration of each hydrocarbon present in the sample is determinable by integrating the area under the individual peak with a planimeter. A close estimate of the concentration of the various hydrocarbons may be obtained by establishing a constant by determining a comparison of integrated area to peak heights. Thereafter the peak heights of the chart are measured and multiplied by the constant to give the concentration of each hydrocarbon.

The concentration of hydrocarbons having from two through seven carbon atoms is determined by one of the methods provided above, and the concentrations are usual-

ly indicated in parts per billion (p.p.b.) of sample. Because the invention is not concerned with absolute hydrocarbon content of any one sample but rather with the relative content, extreme accuracy in the analysis of any given sample is not important in the method since an anomaly indicative of a commercial underground petroleum accumulation may have values from 3 to 1000 times that of the background samples from surrounding area. However, the method must have very high sensitivity because frequently the average amount of hydrocarbons from the samples is less than one p.p.b. The method of separation and analysis of the present invention has a sensitivity of less than one part per trillion (p.p.t.) of weight of hydrocarbon to weight of sample.

To determine the likelihood of the presence of subterranean petroleum deposits using the method of the invention, the hydrocarbon content of the individual hydrocarbons of each sample containing from two through five carbon atoms are totaled, and the hydrocarbons containing six and seven carbon atoms are totaled. These totals may be arrived at, for example, by integrating the areas under the separate peaks with a planimeter such as described above. For convenience the hydrocarbons will be abbreviated by referring to a hydrocarbon by the number of carbon atoms it contains, i.e., C_6 is a hydrocarbon containing six carbon atoms. The p.p.b. of the C_2–C_5 hydrocarbons are totaled, and the p.p.b. of the C_6–C_7 are totaled. This is important in distinguishing an anomaly which is indicative of natural subterranean petroleum accumulations from an anomaly which is caused by surface contamination.

For example, it has been found that if a sample contains many p.p.b. of the C_6–C_7 hydrocarbons in relation to a very few p.p.b. of the C_2–C_5 hydrocarbons surface contamination should be suspected. Since many of the samples are obtained in areas where refined petroleum products are available, the samples can be contaminated by these products. Refined petroleum products contain relatively large amounts of C_6–C_7 hydrocarbons compared to the amounts of C_2–C_5 hydrocarbons. Therefore, a sample having a large amount of C_6–C_7 hydrocarbons and no, or relatively little, C_2–C_5 hydrocarbons would be suspected of being false due to refined product contamination. On the other hand natural petroleum accumulations generally have a more balanced hydrocarbon content in the range from C_2 through C_7 hydrocarbons. In the case of petroleum seeps, the light gas distribution normally is methane greater than ethane greater than propane greater than butanes, etc.

A high reading in the C_2–C_5 hydrocarbons with no corresponding high in C_6–C_7 hydrocarbons from a sample gives rise to the suspicion that the C_2–C_5 hydrocarbons may be from gases and not from heavier petroleum products. This type of reading, i.e., high in C_2–C_5 hydrocarbons with very small amounts of C_6–C_7 hydrocarbons, can be an indication of valuable gas deposits. However, commercial petroleum accumulations are more likely to be indicated by anomalies having highs in both C_2–C_5 hydrocarbons and C_6–C_7 hydrocarbons.

Referring now specifically to FIG. 3, a map showing the boundaries of known underground petroleum deposits is shown. The boundaries of the deposits were determined by means well known in the oil recovery art. Also shown on the map are locations of surface or near-suface sampling points. These sampling locations are shown in the form of small black dots such as dots **121**. The concentration of hydrocarbons found in the sample collected at each location is plotted for each dot. The concentration of C_2 through C_5 hydrocarbons are totaled and plotted as a solid line on the left edge of the dot and the concentration of C_6–C_7 hydrocarbons are totaled and plotted as a dashed line on the right edge of each dot. A scale of parts per billion is shown on the left of FIG. 3.

The samples were collected, preserved, and analyzed according to the method of the present invention. The anomaly occurring over the known petroleum deposits is clearly seen in FIG. 3 in both the C_2–C_5 hydrocarbons and the C_6–C_7 hydrocarbons. The anomaly contrast is much less however for the C_6–C_7 hydrocarbons than for the C_2–C_5 hydrocarbons. It is interesting to note the anomaly at the sample locations indicated by **122** in the south-southeast portion of the map where no deposit of petroleum is known. This anomaly is suggestive of a subsurface source of petroleum and would be a very likely location for a test well.

FIG. 4 is a map showing the boundaries of known subsurface petroleum gas deposits. The locations where samples were collected are indicated as dots. The samples were taken at or near the surface of the earth. The samples were preserved and analyzed according to the present invention. Excellent anomaly contrast is shown over the known petroliferous deposit. The concentration of C_2–C_5 hydrocarbons is indicated by the solid line extending from the left side of each dot. The C_6–C_7 hydrocarbon content for the sample collected at each location is shown by the dashed line extending from the right of each dot. A likely location of additional petroliferous deposits is indicated by the high C_2–C_5 hydrocarbon content and the C_6–C_7 hydrocarbon content of the samples located directly west of the known body. Heretofore, there was no known petroleum deposit at this location. The results shown graphically in the maps of FIG. 3 and FIG. 4 are plotted from actual field samples obtained and analyzed by the method of the present invention. The location of the known petroliferous deposits and the surface locations of the anomalies are not given for obvious reasons.

In test results of the method, the C_2–C_5 hydrocarbon fraction has provided the best anomalies. If high concentrations of C_6–C_7 hydrocarbons are found in a sample with low concentrations of C_2–C_5 hydrocarbons, the results are suspect. A fresh sample should be obtained from the location if possible. Either the original sample has been contaminated by (1) a refined product such as gasoline or (2) a weathered crude oil or the sample has lost the C_2–C_5 hydrocarbons during collection, shipping, or storage. The complete hydrocarbon analysis from ethane (two carbon atom hydrocarbons) to heptane and toluene (seven carbon atom hydrocarbons) makes the method of the present invention superior to methods heretofore practiced.

From the foregoing description it is noted that heretofore unknown subterranean petroliferous deposits can be located by taking surface or near-surface samples, preserving the hydrocarbon content of the samples, and analyzing them according to the method of the invention. Variations and modifications may be made in the details of the method without departing from the invention. All such modifications and changes coming within the scope of the appended claims are intended to be included therein.

What is claimed is:

1. A method of determining the presence of a subterranean deposit of petroleum by analyzing samples for the presence therein of minute quantities of hydrocarbons comprising collecting a plurality of water samples from laterally spaced-apart surcace and near-surface locations of the earth, analyzing each of said samples for the presence of hydrocarbons containing from two through seven carbon atoms, plotting separately on a map at a position corresponding to the location of the earth above where each sample was collected the total concentration of hydrocarbons having from two through five carbon atoms and the total concentration of hydrocarbons having six and seven carbon atoms and drilling an exploratory well at a location of the earth corresponding to a location on said map where anomalous highs in both hydrocarbons having from 2 to 5 carbon atoms and hydrocarbons having 6 and 7 carbon atoms occur.

2. A method of determining the presence of a subter-

ranean deposit of petroleum by analyzing samples for the presence therein of minute quantities of hydrocarbons comprising collecting a plurality of water samples from laterally spaced-apart surface and near-surface locations of the earth, adding a bactericide to each of said samples when it is collected to prevent destruction by bacteria of any hydrocarbons contained in said samples, subjecting each of said samples to evaporative conditions in the presence of a carrier gas to remove from each of said samples any hydrocarbons contained therein, analyzing said hydrocarbons from each of said samples for the presence of hydrocarbons containing from two through seven carbon atoms, plotting the concentration of hydrocarbons having from 2 through 5 carbon atoms and the concentration of hydrocarbons having 6 and 7 carbon atoms on a map at a position corresponding to the location on the earth where the sample was collected and drilling an exploratory well at a location on the earth corresponding to a location on said map where anomalous highs in both hydrocarbons having from 2 through 5 carbon atoms and hydrocarbons having 6 and 7 carbon atoms occur.

3. A method of determining the presence of subterranean petroliferous deposits by analyzing liquid samples for the presence therein of minute quantities of hydrocarbons comprising collecting water samples from laterally spaced-apart surface and near-surface locations of the earth, analyzing said hydrocarbons from each of said samples for the presence of hydrocarbons containing from two through seven carbon atoms, plotting separately on a map at a position corresponding to the location on the earth where the sample was collected the total concentration of hydrocarbons having from two through five carbon atoms and the total concentration of hydrocarbons having six and seven carbon atoms and drilling an exploratory well at a location on the earth corresponding to a location on said map where anomalous highs in both hydrocarbons having from two through five carbon atoms and hydrocarbons having six and seven carbon atoms occur.

4. A method of determining the presence of subterranean petroliferous deposits by analyzing liquid samples

for the presence therein of minute quantities of hydrocarbons comprising collecting water samples from spaced-apart surface and near-surface locations of the earth, adding a bactericide to each of said samples when it is collected to prevent destruction by bacteria of any hydrocarbons contained in said samples, analyzing said hydrocarbons from each of said samples for the presence of hydrocarbons containing from two through seven carbon atoms, plotting separately on a map at a position corresponding to the location on the earth where the sample was collected the total concentration of hydrocarbons having from two through five carbon atoms and the total concentration of hydrocarbons having six and seven carbon atoms and drilling an exploratory well at a location on the earth corresponding to a location on said map where anomalous highs in both hydrocarbons having from two through five carbon atoms and hydrocarbons having six and seven carbon atoms occur.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,345,137 October 3, 1967

Clayton D. McAuliffe

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 13, for "removed" read -- remove --; column 3, lines 41 to 43, strike out "FIG. 4 is a map showing the boundaries of known underground petroleum accumulations and the hydrocarbon content of the samples collected from the area."; columns 5 and 6, in the table, in the sub-heading to column 6 thereof, for "N-Penatne" read -- N-Pentane --; same table, seventh column, line 10 thereof, for "(1)" read -- (2) --; column 5, line 71, for "C_1 and C_7" read -- C_1 through C_7 --; column 8, line 24, for "hydrocarbon" read -- hydrocarbons --; column 10, line 62, for "surcace" read -- surface --; lines 66 and 71, for "of", each occurrence, read -- on --; line 73, for "to" read -- through --.

Signed and sealed this 22nd day of October 1968.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

EDWARD J. BRENNER
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