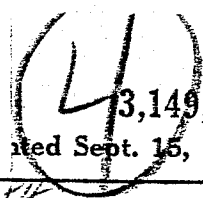


United States

TX 9200 N


 3,149,068
 Filed Sept. 15, 1964

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3,149,068

GEOCHEMICAL EXPLORATION

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No Drawing. Filed Mar. 8, 1961, Ser. No. 94,168
 5 Claims. (Cl. 210-31)

This invention relates to geochemical exploration and more particularly to the analysis of earth samples to determine the proximity of petroleum deposits.

Various geochemical methods have been suggested previously for determining the location of underground petroleum reservoirs. These methods are intended to detect the presence of petroleum constituents in surface or underground formations in greater than normal quantity. Such anomalies are taken as an indication of the proximity of a petroleum reservoir or other concentration of petroleum type hydrocarbons. It is thus possible, by detecting the presence of petroleum constituents in earth samples such as soil or rock samples, to ascertain the location and proximity of petroleum deposits by correlating the relative amounts of petroleum constituents present in the earth samples with the locations from which the samples were taken.

It has been suggested previously that the presence of petroleum constituents in an earth sample may be detected by extracting organic constituents from the earth sample and then evaluating the fluorescence of the extract or a concentration thereof under ultraviolet light. These methods depend upon the known fluorescence of certain petroleum constituents, especially intermediate aromatics. One such method is described in U.S. Patent 2,451,883. While methods of this type for determining the presence of petroleum constituents by fluorescence of earth samples or concentrated extracts thereof have met with some degree of success, such methods have frequently failed to provide the desired information because it has been impossible to distinguish the fluorescence due to the desired petroleum constituents from fluorescence due to other organic constituents.

While certain petroleum constituents, especially the lighter aromatics normally found in petroleum, fluoresce strongly in the light blue range under ultraviolet radiation, numerous other organic compounds which do not necessarily indicate the presence of petroleum (although they may also be present in petroleum) also fluoresce under ultraviolet light, some of them in the same color range. For instance, extracts of coals, coal-like materials and chlorophylls all fluoresce under ultraviolet light but are not an indication of the presence of petroleum. More specifically, anthracene type materials fluoresce with a light blue color and are readily extracted from soft coal and anthracite. Where the anthracene is oxygenated and occurs as anthraquinone, it also fluoresces blue. Organic acids and cresols likewise contribute to the overall fluorescence of earth samples. Crude oils, however, contain much less of these materials than do shales, especially oil barren shales. If a sufficiently strong solvent is used to extract substantially all of the desired petroleum constituents, then any of these undesirable fluorescent organic constituents present in the sample will be extracted along with the desired petroleum constituents. Previously known methods for determining the presence of petroleum constituents by fluorescence of earth samples or extracts therefrom have been unable to discriminate between the various types of fluorescent materials mentioned above.

It is an object of the present invention to provide an improved method of geochemical exploration to determine the proximity of petroleum deposits.

Another object of the invention is to provide a novel method for detecting the presence of petroleum constituents in earth samples.

It has now been found that the presence of petroleum constituents in earth samples may be determined with a high degree of accuracy by first applying chromatographic separation techniques to separate from the earth sample those constituents which are not mobile in polar chromatographic carrier solvents but which are mobile in non-polar chromatographic carrier solvents. The fluorescence of these constituents is then checked to determine the presence of fluorescent petroleum constituents in the earth sample.

Any suitable chromatographic technique may be used in separating constituents of earth samples in accordance with the present invention. For instance, the separation may be effected in a combination of chromatographic columns packed with suitable chromatographic adsorption material such as cellulose, alumina gel, silica gel, etc. While column chromatography or suitable combinations of other one dimensional chromatographic techniques may be used, it is highly advantageous to utilize two dimensional chromatography in obtaining the desired separation of constituents from the earth samples. In two dimensional chromatography, the sample being analyzed is placed on chromatographic adsorption material and driven in two different directions by two different carrier solvents. Due to their different adsorption characteristics with respect to the adsorption material and solvents, the various constituents of the sample are carried varying distances along the adsorption material in each direction before being deposited thereon from solution with the carrier. While any suitable bed of chromatographic adsorption material may be used, the use of a relatively thin layer of material is preferred. Special chromatographic paper or ordinary filter paper is especially suitable for this purpose. Two-dimensional chromatography using a relatively thin layer of chromatographic adsorption material such as filter paper is preferred in practicing the present invention for two reasons. First, this technique requires extremely small quantities of extract sample and can thus be used to analyze small earth samples. This, of course, facilitates collection and transportation of samples as well as analysis and storage of samples and completed chromatograms. In addition, this technique, especially in the form described below, is very simple and readily adaptable to field conditions, requiring only a minimum of simple, rugged equipment and small quantities of supplies.

In applying two dimensional chromatography to the practice of a preferred embodiment of the present invention, the earth sample being analyzed is first treated with suitable solvent to extract organic constituents including the desired petroleum constituents therefrom. This extract is then deposited on chromatographic adsorption material such as ordinary filter paper and the solvent is preferably at least partially evaporated. A polar chromatographic carrier solvent is then introduced into the adsorption material and passes therethrough by adsorption. Constituents mobile in the polar carrier solvent are thus separated from the deposited extract and moved along the adsorption material in the direction taken by the carrier. A non-polar carrier solvent is then introduced into the adsorption material so as to pass through the adsorption material in a direction perpendicular to the path of the polar solvent. The non-polar solvent thus moves constituents of the deposited extract which are mobile in the non-polar solvent along the adsorption material in the direction of movement of the non-polar solvent. The fluorescence of any of the thus separated constituents of the earth sample may then be evaluated by suitable means such as the use of a standard ultraviolet light. It should be understood

that either the polar or the non-polar solvent may be used first so long as the second solvent passes through the adsorption material in a direction non parallel and preferably perpendicular to the direction of movement of the first solvent. While the order in which the polar and non-polar solvents are employed is not critical, it has been found that somewhat sharper separations of various constituents are obtained when the polar solvent is used first and the use of a polar carrier solvent followed by a non-polar carrier solvent as described above is, therefore, preferred.

As a matter of convenience in using the two dimensional chromatographic techniques described above and in discussing the results obtained with such techniques it has been found desirable to deposit the extracted organic constituents of the earth sample on the corner of a square or rectangular piece of filter paper and arbitrarily refer to the various portions of the filter paper with reference to the position of the filter paper when the deposited extract is in the lower right hand corner thereof. This practice will be followed herein.

A wide variety of organic solvents are suitable for extracting organic constituents from earth samples in the practice of the present invention. It is preferred, however, to use solvents sufficiently strong to insure that all of the desired fluorescent petroleum constituents are extracted from the sample. If all these constituents are not extracted, the quantitative analytical results will, of course, be somewhat in error. To insure that substantially all of the constituents are extracted, the organic solvent used is preferably one which is sufficiently strong to dissolve asphaltic material. These may be referred to as strong organic solvents. For this purpose asphaltic material may be defined as hydrocarbon material which is not soluble in pentane. Suitable strong solvents include, for instance, benzene, toluene, xylene, carbon tetrachloride, diethyl ether, ethyl acetate, etc. or combinations of these with polar solvents such as isopropyl alcohol or acetone.

Likewise, any suitable polar and non-polar carrier solvents may be used in practicing the present invention. In order to cause all of the desired constituents to migrate without having an excessive amount of the relatively heavier asphaltic material migrate, it is preferred that both the polar and non-polar carriers be relatively weak carriers which are not sufficiently strong to cause migration of asphaltic material as defined above. These may be referred to as weak polar and non-polar carrier solvents. Use of overly strong carrier solvents tends to cause migration of asphaltic material which then masks the presence of the desirable constituents, especially the lighter aromatics. Suitable weak polar carrier solvents include, for instance, methanol, ethanol, acetone or mixtures of these with small amounts of water.

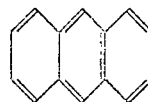
Suitable non-polar carrier solvents include, for instance, straight chain hydrocarbons having at least 5 carbon atoms, branched chain paraffins, cycloparaffins, etc. Among the polar carrier solvents methanol has been found especially suitable while among the non-polar carrier solvents hexane, heptane and octane have been found especially suitable.

When organic constituents extracted from earth samples are deposited on the corner of a sheet of filter paper as described above and the polar carrier solvent is introduced by placing the lower edge of the filter paper in the solvent so as to cause the same to move upwardly through the filter paper and the non-polar carrier solvent is then introduced by placing the right hand edge of the filter paper in the non-polar carrier solvent so that it moves to the left across the filter paper, then the desired fluorescent petroleum constituents which are mobile in the non-polar solvent but immobile in the polar solvent will be found along the lower edge of the filter paper or chromatogram. It is obvious that the distance from the original deposit at which these constituents will be found depends upon the amount and concentration of the carrier solvent uti-

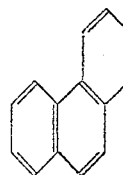
lized as well as on the relative adsorption characteristics of the solvent and of the specific constituents. The following description of various constituents found in various corners of squares of filter paper following analysis of the type described above is based on the assumption that sufficient quantities of carrier solvents are utilized to drive the majority of such compounds which are mobile in the particular solvent involved substantially the entire width of the filter paper. If the analysis is carried out in this fashion the various constituents will be grouped substantially at the corners of the filter paper. The following compounds are typical of those which will be found at the various corners of the filter paper when the required chromatographic separation has been accomplished in the arbitrary manner described above using methanol as the polar carrier solvent and heptane as the non-polar carrier.

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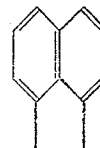
Anthracene



Phenanthrene

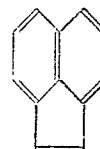


Acenaphthene

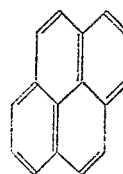


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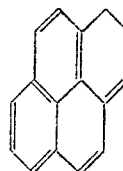
Acenaphthylene



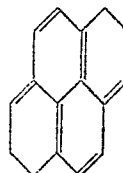
Pyrene



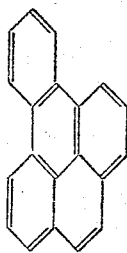
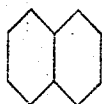
Dihydropyrene



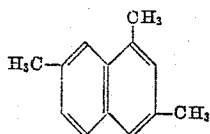
Tetrahydropyrene



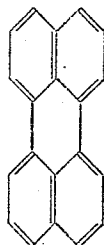
1,2-benzpyrene

Decalin, $C_{10}H_{18}$ 

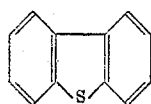
1,3,7-trimethylnaphthalene



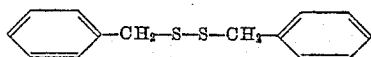
Perylene



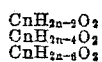
Dibenzothiophene



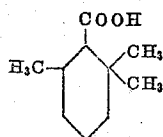
Benzyl disulfide



Naphthenic acids

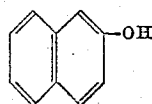


One example:

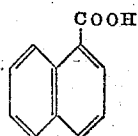
 C_5-C_{13} paraffins

2-naphthol

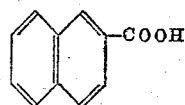
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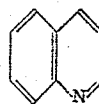
1-naphthoic acid



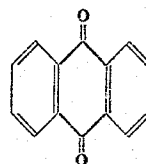
2-naphthoic acid



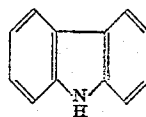
Quinoline



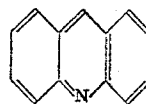
Anthraquinone



Carbazole



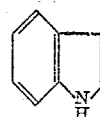
Acridine



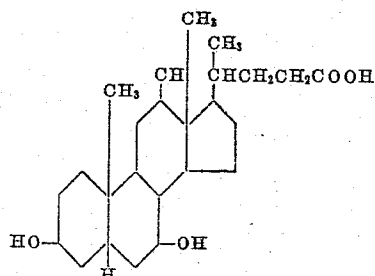
Pyrrole



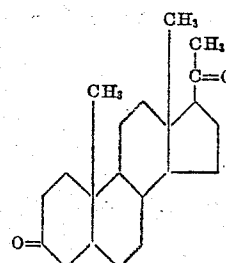
Indole



Cholic acid

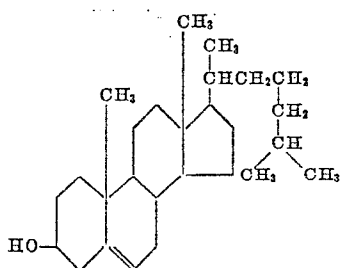


Progesterone

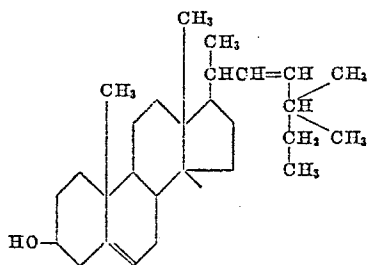


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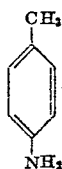
Cholesterol



Stigmasterol



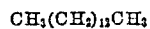
p-Toluidine



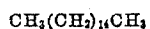
Methanol mobile heptane immobile fraction of crude oil
Methanol mobile heptane immobile fraction of shale
extract

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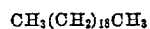
Tetradecane



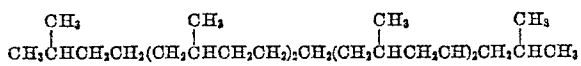
Hexadecane



Eicosane



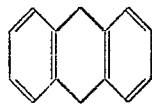
Squalane



Nujol heavy mineral oil

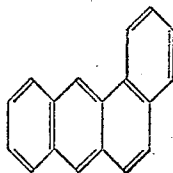
Average mol. wt. 547

9,10 dihydroanthracene



1,2-benzathracene

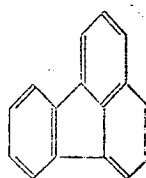
Aldrich Chemical



Fluoranthene

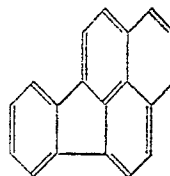
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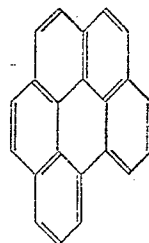
10 3,4-benzofluoranthene

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20 1,12-benzoperylene

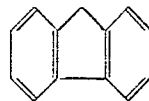
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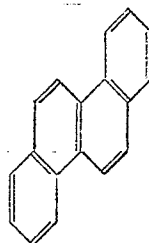
Fluorene

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40 Chrysene

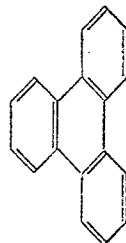
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Triphenylene

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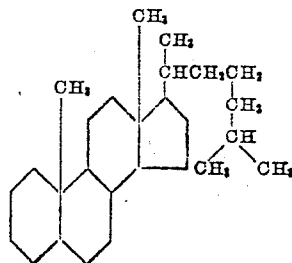
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Cholestane

65

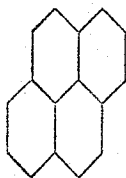
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Perhydropyrene

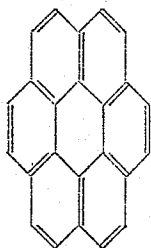


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p-Terphenyl



Coronene



By applying the chromatographic separation techniques described above to a number of earth samples taken from selected locations it is possible to correlate the presence and quantity of petroleum constituents found in each sample with the location from which the sample was taken in order to determine the presence and proximity of petroleum bearing shale or sand, with respect to such location. For the results to have relative meaning with respect to a number of samples from the same general area it is necessary only that the different samples be subjected to the same treatment. For the results to have any quantitative meaning it is also necessary to have available comparative chromatograms based on known petroleum bearing formations. By preparing sets of standardized chromatograms using an arbitrarily standardized technique of the type described above and utilizing earth samples from known locations in reference to known petroleum deposits, it is possible to compare the fluorescence of the appropriate portion of the chromatograms obtained from the earth samples in question with the reference chromatograms in order to obtain quantitative data respecting the presence of petroleum deposits in the area from which the samples in question were taken. For best results fresh reference standards should be prepared at frequent intervals, preferably weekly, because the lighter aromatics in the fluorescent petroleum fraction exhibit decreasing fluorescence with time.

Example 1

In the practice of previously known geochemical methods for determining the presence of oil constituents in earth samples by fluorescence, oxygen containing compounds have been responsive for much of the confusion between fluorescent petroleum constituents and other fluorescent constituents of the earth samples. In order to demonstrate that the method of the present invention separates these compounds from petroleum constituents, a sample of crude oil containing both oxygenated compounds and petroleum constituents not containing oxygen was fractionated into 65 fractions by column chromatography using a series of carrier solvents (e.g., petroleum ether, benzene, CCl_4 , acetone, etc.). Each of these fractions was then subjected both to infrared spectra analysis and to chromatographic separation using methanol carrier solvent (a polar carrier). In every case where an oxygen band was observed in the infrared pattern, a fluorescent fraction mobile in methanol was observed on the

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chromatogram. Conversely, in every case where there was no indication of oxygen in the infrared pattern, there was no fluorescent methanol mobile fraction on the chromatogram.

- 5 Detection of fluorescent petroleum constituents in accordance with the present invention is not, therefore, confused by the presence of oxygenated compounds in the earth sample.

Example 2

- 10 To further evaluate the method of the present invention, earth samples from a number of known formations were analyzed by the following procedure: In each case the earth sample was pulverized with a mortar and pestle (so that all of the sample passed through a size 50 sieve (U.S. sieve series). Two grams of this material were placed in a small screw cap vial and 2 milliliters of a 1:1 solution of isopropyl alcohol and toluene were added with a pipette. The sample vial was then capped tightly, shaken vigorously for 1 minute and allowed to settle at room temperature. Best results were obtained when the vials were agitated 3 times in 24 hours, with care being taken after the third agitation to wash the sediment from the sides of the vial to insure that all solids were in contact with the solvent. The sample was then allowed to settle until the solution above the sediment was clear. $\frac{1}{100}$ of a milliliter of the extract was then drawn into a micropipette and evaporated onto the corner of a 1 inch square piece of chromatographic paper (Whatman No. 1). The margins of the corner spot were confined to an area 5 millimeters on a side. A gentle air stream directed onto the area of evaporation was found to be helpful in speeding up the evaporation of the solvent. One edge of the 1 inch square paper containing the evaporated spot of extract (the lower edge according to the arbitrary procedure discussed above) was then placed in methanol and the methanol was allowed to migrate upwardly for a distance of $\frac{1}{2}$ inch. The paper was then dried in air and the other edge containing the spot (the right hand edge) was placed in heptane which was allowed to migrate at right angles to the methanol migration. The effect of this was to separate the extract constituents in the manner discussed above with fluorescent petroleum constituents mobile in heptane (non-polar carrier solvent) but immobile in methanol (polar carrier) spread out along the bottom edge of the paper. After the paper was dry it was examined under a high intensity ultraviolet light (3660 A.) and the intensity of the fluorescence on various portions of the paper was noted and interpreted as described above. In the case of known oil bearing formations the fluorescence of the fluorescent petroleum constituents was compared with reference standards prepared from related crude oils. In addition, each of the earth samples tested was also tested in accordance with the prior art techniques by examining the total extract from the earth sample under the same ultraviolet light.

When tested by mere examination of total extract under ultra-violet light as described above and suggested by the prior art, earth samples from each of the following formations (known to contain little or no petroleum hydrocarbons) exhibited strong fluorescence.

Age	Formation	Basin	State
Cretaceous	Graneros	Salina	Kansas.
Cambro-Ordovician	Arbuckle	Oherokee	Do.
Ordovician	Viola	Forest City	Do.
Devono-Silurian	Hunton	do	Do.
Permian	Blain	Salina	Do.
Cretaceous	Frontier	Shirley	Wyoming.

Further analysis of these samples in accordance with the present invention and as described above indicated, however, that the fluorescent constituents of these samples were not petroleum constituents.

Earth samples from the following rock formations were also analyzed as described above.

Age	Formation	Basin	State
Permian.....	San Andres.....	Palo Duro.....	Texas.
Do.....	do.....	Permian.....	Do.
Do.....	Glorieta.....	do.....	Do.
Do.....	Clearfork.....	do.....	Do.
Do.....	Wichita.....	do.....	Do.
Do.....	Wolfcamp.....	Palo Duro.....	Do.
Pennsylvanian.....	Cisco.....	do.....	Do.
Do.....	Canyon.....	Permian.....	Do.
Do.....	Strawn.....	do.....	Do.
Do.....	Bend.....	do.....	Do.
Do.....	Cherokee.....	Forest City.....	Kansas
Do.....	Oread.....	do.....	Do.
Do.....	Kansas City.....	do.....	Do.
Cretaceous.....	Mowry.....	Wind River.....	Wyoming.

In each case the extracts from these earth samples fluoresced strongly while analysis in accordance with the present invention disclosed that the fluorescent material was actually composed partly of fluorescent petroleum constituents and partly of fluorescent constituents not indicating the presence of petroleum. This was in accordance with known facts concerning these formations. In the case of these earth samples mere examination for fluorescence correctly indicated the presence of petroleum constituents but gave completely erroneous information concerning the relative quantities of such constituents since, except by the application of the present invention, it was impossible to determine how much of the fluorescence was attributable to petroleum constituents and how much to non-petroleum indicating constituents.

The above examples indicate clearly that the process of the present invention is capable of distinguishing between those fluorescent constituents of earth samples which indicate the presence of petroleum and those fluorescent constituents which may or may not be present in petroleum but which do not necessarily indicate the presence of petroleum.

While the invention has been described above in connection with certain preferred embodiments thereof, it will be understood by those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the invention and it is intended to cover all such changes and modifications in the appended claims.

We claim:

1. A geochemical exploration method for determining the proximity of an underground petroleum reservoir which comprises collecting earth samples from various locations in an exploration zone, similarly and separately treating said samples by contacting them with strong organic solvent to extract organic constituents including desired petroleum constituents therefrom, chromatographically fractionating each sample to separate therefrom fluorescent petroleum constituents mobile in a weak non-polar carrier solvent and immobile in a weak polar carrier solvent, subjecting thus separated constituents to ultraviolet radiation, and correlating the relative fluorescence of the fluorescent petroleum constituents separated from each sample with the locations from which such samples were taken.

2. The method for separating fluorescent petroleum

constituents which are mobile in a weak non-polar chromatographic carrier solvent and immobile in a weak polar chromatographic carrier solvent from an earth sample containing the same which comprises contacting the earth sample with a strong organic solvent to extract organic constituents including the desired petroleum constituents therefrom, depositing thus extracted organic constituents on chromatographic adsorption material, and treating thus deposited organic material with a weak polar and a non-polar carrier solvent by first passing one of said carrier solvents in one direction through the adsorption material to thereby separate fractions of the organic constituents mobile in such carrier and then passing the second of said carriers through the chromatographic adsorption material in a direction non parallel to the path of the first of said carriers to thereby separate fractions mobile in said second carrier.

3. The method according to claim 2 in which the organic solvent is a mixture of isopropyl alcohol and acetone, the polar solvent is methanol and the non-polar solvent is heptane.

4. The method for separating fluorescent petroleum constituents which are mobile in a weak non-polar chromatographic carrier solvent and immobile in a weak polar chromatographic carrier solvent from an earth sample containing the same which comprises contacting the earth sample with a strong organic solvent to extract organic constituents including the desired petroleum constituents therefrom, depositing thus extracted organic constituents on chromatographic adsorption material, and treating thus deposited organic material with a weak polar and a weak non-polar carrier by first passing one of said carriers in one direction through the adsorption material to thereby separate fractions of the organic constituents mobile in such carrier and then passing the second of said carriers through the chromatographic adsorption material in a direction generally perpendicular to the path of the first of said carriers to thereby separate from said first fractions those fractions mobile in said second carrier.

5. The method of determining the presence of fluorescent petroleum constituents in an earth sample containing the same and other fluorescent organic constituents which comprises contacting the earth sample with a strong organic solvent to extract organic constituents including the desired petroleum constituents and other undesired fluorescent constituents therefrom, depositing thus extracted organic constituents on chromatographic adsorption material, passing a weak polar chromatographic carrier solvent through said adsorption material in one direction to thereby separate from the deposited organic constituents fractions mobile in said polar carrier, passing a weak non-polar chromatographic carrier solvent through said adsorption material in a direction generally perpendicular to the path of the polar carrier to thereby separate fractions mobile in the non-polar carrier and subjecting thus separated fractions to ultraviolet radiation.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,149,068

September 15, 1964

Edwin W. Biederman, Jr., et al.

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 9, line 34, after "of" insert -- petroleum deposits, such as reservoirs or --; line 61, for "responsive" read -- responsible --.

Signed and sealed this 12th day of January 1965.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents