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# METHOD OF GEOCHEMICAL EXPLORATION BY THE INFRARED ANALYSIS OF SELECTED ATOMS OF ISOLATED AROMATIC HYDROCARBONS

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## ABSTRACT OF THE DISCLOSURE

This specification discloses a geochemical exploration method in which a sample obtained from an organic matter-containing formation in the earth's crust is analyzed for the relative concentration of hydrogen atoms on aromatic nuclei having one or more hydrogen atoms but not more than two adjacent hydrogen atoms attached thereto and the relative concentration of hydrogen atoms on aromatic nuclei having four or five adjacent hydrogen atoms attached thereto. The ratio of the relative concentrations of these two classes of hydrogen atoms is indicative of the likelihood of the formation being a petroleum source rock.

This invention relates to geochemical exploration for petroleum minerals, and more particularly to a geochemical exploration method which involves the identification of petroleum source rock formations on the basis of the distribution of certain aromatic hydrocarbon structures.

Petroleum is found in commercial quantities in subsurface rock formations, such as sandstones and limestones. The presence of a petroleum deposit in a subterranean formation is not ordinarily manifested by readily discernible indicia at the earth's surface. Accordingly, various techniques have been evolved in exploring for oil. Among these are those which fall within the general classification of geochemical exploration.

In most geochemical exploration techniques, a search is made, usually at or near the surface of the earth, for components of petroleum, precursors of petroleum, or derivatives thereof. These procedures are based upon the theory that these materials may have migrated to or near the surface of the earth from an underlying petroleum reservoir. Thus, where materials, such as hydrocarbons, which are normally constituent components of petroleum are found, the presence of a subterranean reservoir of petroleum in the area is indicated. A valuable geochemical exploration technique is described in U.S. Patent No. 2,742,572 to E. E. Bray. This process is based upon the discovery that the infrared spectra for crude oil exhibits definite absorption bands in the regions of about 12.4 microns and 13.4 microns. Therefore, in accordance with the procedures described in this patent, earth samples are extracted to obtain extracts containing organic matter and these extracts are subjected to infrared spectrometry in order to determine the presence or absence of absorption bands in the aforesaid regions. Extracts exhibiting infrared absorption bands within these regions are considered to be an indication of the possible presence of subterranean petroleum deposits within the area under investigation.

While techniques, such as the one described in the aforementioned patent to Bray, are extremely valuable in determining the presence of petroleum within a general area, they usually give little indication of the precise location of the underlying petroleum reservoir. Other exploration procedures such as seismic surveying may be utilized to identify possible petroleum reservoirs at subterranean locations in the earth's crust. However, while such measures may give valuable information as to subterranean structures favorable to the accumulation of petroleum, they leave much to be desired in regard to determining which, if any, of such structures actually contain petroleum deposits.

In attempting to ascertain whether such structures contain petroleum, geologists have in recent years turned to exploration techniques based upon the so-called "source rock" concept. Under this concept, it is assumed that petroleum hydrocarbons are formed during long periods of burial in sediments of high organic matter content, the petroleum hydrocarbons being derived from organic matter of biologic origin which was deposited with these sediments in a marine environment. The exact mechanism by which oil is formed within such sediments, i.e., source rocks, is not known with certainty. After the oil-forming mechanism has taken place, it is thought that the petroleum hydrocarbons in the source rock then migrated to more permeable reservoir rocks where they accumulated in the concentrated deposits found today.

One important series of compounds found in petroleum oils are the normal paraffins. Most crude oils contain approximately equal concentrations of odd and even carbon number paraffins with the ratio of odd to even usually falling within the range of about 0.9 to 1.15. On the other hand, most sediments of relatively recent origin exhibit a relatively high ratio of odd carbon number paraffin concentrations to even carbon number paraffin concentrations.

In accordance with this observed distribution of even and odd carbon number paraffins, it has been proposed to locate petroleum source rocks on the basis of this distribution, termed the "carbon preference index," in exploring for petroleum reservoirs. In this regard, it has been proposed to identify petroleum source rocks by the distribution of normal paraffins therein with a rock having a ratio of odd to even carbon number paraffin concentrations near 1.0, i.e., on the order of the ratio found in most paraffin crude oils, being indicated as a source rock. A detailed description of this exploration technique and certain investigations relative thereto may be found in Bray, E. E. et al., "Distribution of Normal Paraffins as a Clue to Recognition of Source Beds," Geochimica et Cosmochimica Acta, 1961, vol. 22, pp. 2–15.

While this technique is a promising tool in the exploration for oil, particularly in the identification of shale source rocks, experience has shown that it is not as reliable as might be desired in the identification of carbonate source rocks. It is believed that many carbonate rock formations, such as mesozoic and paleozoic limestones and dolomites may be possible source rock for petroleum hydrocarbons. Thus, a reliable method for the identification of such carbonate source rocks is a needed tool in petroleum exploration.

In accordance with the instant invention, there is provided a new and improved geochemical exploration technique for the identification of possible petroleum source rocks and which is applicable to carbonate rocks as well as non-carbonate rocks such as shales. This invention is based upon the distribution in source rock type formations of certain aromatic hydrocarbon structures and, more particularly, the abundance of primary hydrogen atoms associated with one class of aromatic hydrocarbon structures having at least one primary hydrogen atom on an aromatic nucleus but not more than two such hydrogen atoms adjacent one another relative to the abundance of primary hydrogen atoms associated with a second class of aromatic hydrocarbon structures having at least four adjacent primary hydrogen atoms but not more than five adjacent primary hydrogen atoms. More particularly, it has been found that the ratio, hereinafter referred to as the "structure distribution index," of the relative concentration of primary hydrogen atoms on aromatic hydrocarbon structures having at least one and no more than two adjacent such hydrogen atoms to the relative concentration of primary hydrogen atoms on aromatic hydrocarbon structures having four or five adjacent such hydrogen atoms, can be used to characterize a rock formation as to the likelihood of its being a source rock for petroleum.

By the term "aromatic hydrocarbon structure," as used herein, is meant an aromatic nucleus which is a structural constituent of an aromatic hydrocarbon molecule including the hydrogen atoms and any substituent groups on the nucleus. The term "primary hydrogen atom" is used herein to designate a hydrogen atom which is attached directly to a carbon atom in the aromatic nucleus. The nucleus of an aromatic hydrocarbon structure may be condensed or noncondensed and the aromatic hydrocarbon may be mononuclear or polynuclear. Thus, by way of example only, diethylbenzene has only a single aromatic hydrocarbon structure whereas naphthalene and anthracene have two and three aromatic hydrocarbon structures, respectively. It is to be noted that both classes of aromatic hydrocarbon structures may be found in the same molecule. For example, in both anthracene and phenanthrene, the two outer benzene rings each have four adjacent hydrogen atoms and therefore fall within the second class of aromatic hydrocarbon structure whereas the center ring has two hydrogen atoms (being adjacent in phenanthrene and nonadjacent in anthracene) and falls within the first class. Thus, these compounds have structure distribution indices of 0.25.

In carrying out the present invention, a sample from a rock formation in the earth's crust is analyzed for the relative concentration of primary hydrogen atoms in aromatic hydrocarbon structures having at least one primary hydrogen atom but not more than two such hydrogen atoms adjacent one another. The rock sample also is analyzed for the relative concentration of primary hydrogen atoms in aromatic hydrocarbon structures having at least four but not more than five adjacent hydrogen atoms on an aromatic nucleus. From the results of this analysis the structure distribution index for the formation may be determined in order to ascertain the probability of the formation being a source rock of petroleum. As will be explained in greater detail hereinafter, in a preferred embodiment of the invention the aromatic hydrocarbon structures from which the structure distribution index is determined are selected on the basis of certain molecular weight criteria. More particularly, these aromatic hydrocarbon structures are constituents of aromatic hydrocarbons having at least ten carbon atoms and preferably at least 18 carbon atoms.

In many cases, it will be preferred to obtain rock samples from a plurality of locations in the earth's crust. The structure distribution indices for these samples are obtained and are correlated with each other and the locations in the earth's crust of their respective samples to ascertain possible source rocks of petroleum hydrocarbons. Thereafter, further exploratory procedures may be undertaken as described below to locate reservoir formations to which petroleum hydrocarbons may have migrated from the designated source rocks.

Infrared absorbance in the regions of 12.4 microns and 13.4 microns, described in the aforementioned patent to Bray, is a function of the relative concentrations of primary hydrogen atoms associated with the above-noted classes of aromatic hydrocarbon structures; provided, that infrared analysis is carried out with regard to aromatic hydrocarbons having at least ten carbon atoms and which are isolated from other organic matter contained in the source rocks. Therefore, in accordance with a preferred embodiment of the invention, aromatic hydrocarbons having at least ten carbon atoms are isolated from an organic matter extract obtained from a rock sample. The aromatic hydrocarbons so isolated then are subjected to infrared spectrometry in the regions of 12.4 microns and 13.4 microns and the infrared absorbance in these regions is measured. The infrared absorbance in the region of 12.4 microns is a function of the relative concentration of primary hydrogen atoms on aromatic hydrocarbon structures having at least one primary hydrogen atom but not more than two primary hydrogen atoms adjacent on an aromatic nucleus and the infrared absorbance in the region of 13.4 microns is a function of the relative concentration of aromatic hydrocarbon structures having four or five adjacent primary hydrogen atoms on an aromatic nucleus. Thus, from the infrared spectrometry data the structure distribution index of the rock sample may be determined.

For a better understanding of the present invention and the objects achieved thereby, reference may be had to the following detailed description.

Structure distribution data for a large group of randomly selected crude oils have shown that the structure distribution indices of these crude oils bear a marked similarity. More particularly, practically all of the crude oils analyzed have structure distribution indices, based upon aromatic hydrocarbons of 18 or more carbon atoms, within the range of approximately 0.8 to 1.4. On the other hand, analyses of a large number of organic matter containing carbonate rock formations have shown a diversity in this relationship, with only a minor part of such formations having structure distribution indices within the aforementioned range and with the majority of such formations having structure distribution indices of less than 0.8. Like the above-mentioned crude oils, the structure distribution indices for these formations were based on aromatic hydrocarbons having 18 or more carbon atoms. On the basis of these investigations, it is postulated that rock formations, and in particular carbonate rock formations, having a structure distribution index of 0.8 or more are likely source rocks of petroleum hydrocarbons.

As noted previously, it is preferred in carrying out the invention to determine the structure distribution index for a rock sample on the basis of aromatic hydrocarbons having at least 18 carbon atoms. The determination of the structure distribution index on the basis of aromatic hydrocarbons having less than 18 carbon atoms is subject to error for a number of reasons. Significant quantities of such lower molecular weight hydrocarbons may be lost from the sample during handling and processing due, for example, to their relative volatility, thus leading to erroneous results. Also, the low molecular weight aromatic hydrocarbons are relatively soluble in water in comparison to heavier aromatics and thus are subject to leaching from the rock formation by the action of subsurface waters.

Notwithstanding the limitations noted above, the instant invention may be carried out with regard to aromatic hydrocarbons having less than 18 carbon atoms to obtain the structure distribution index. However, if, as is preferred in carrying out the invention, infrared spectroscopy is used to determine the relative abundance of primary hydrogen atoms associated with the classes of aromatic hydrocarbon structures of interest, a lower molecular weight limit of at least ten carbon atoms should be observed. In this regard, the inclusion of aromatic hydrocarbons having less than ten carbon atoms in the sample subject to analysis by infrared spectroscopy will render the resulting spectrogram complex and difficult to interpret in certain critical areas. Thus, in carrying out the preferred embodiment of the invention, analysis is made by infrared spectrometry and the aromatic hydrocarbons subjected to infrared analysis have at least ten carbon atoms. Preferably, for the reasons mentioned beforehand, these aromatic hydrocarbons have at least 18 carbon atoms.

An analysis of the rock sample with regard to the aromatic hydrocarbon structures may be carried out by any suitable procedure. However, care must be taken to employ a procedure which will yield accurate results since the aromatic hydrocarbon concentrations in such rocks normally will be relatively low. For example, petroleum source rocks normally have an organic matter content on the order of six percent by weight or less for shales and one percent by weight or less for carbonates with only a relatively minor amount, e.g., on the order of ten percent by weight or less of this organic content actually comprising aromatic hydrocarbons.

In a preferred procedure for analyzing for aromatic hydrocarbon structure distribution, the rock sample is dried and crushed to obtain a homogeneous mixture. This may be accomplished by drying the sample for a suitable period of time, e.g., a period of approximately five days at 100° F., and then pulverizing the sample so that it passes a 14 mesh sieve.

The crushed rock sample then is extracted by a suitable solvent in order to obtain an organic matter extract. A satisfactory solvent is a mixture of ten parts benzene and one part methanol. This solvent mixture may be added to the pulverized rock sample in an amount of 165 milliliters of solvent for 150 grams of rock sample. The sample solvent mixture then may be extracted by a ball mill technique in which it is subjected to agitation at a temperature of about 70° F. for a period of about four hours. The extracted solution then is recovered by decantation and, if necessary, centrifuging. The extract then may be filtered by any suitable procedure in order to remove any insoluble material remaining. If desired, a small amount of water, e.g., 35 milliliters, may be added prior to decantation in order to aggregate soil particles in suspension and also to remove methanol from the solvent.

At this stage of the procedure, the extract may be treated to remove the lower molecular weight aromatic hydrocarbons. This may be accomplished by placing the extracted solution in an evaporator bath and passing air over the solution at a temperature of 40° C. until a dry residue remains. After the dry residue is weighed, it is placed in solution with benzene, and the resulting solution is again evaporated to dryness as before. This procedure is repeated until the residue reaches a constant weight. By this procedure, substantially all of the aromatic hydrocarbons having 17 or less carbon atoms are removed from the organic residue which includes the heavier aromatics.

The extract thus far recovered will contain, in addition to aromatic hydrocarbons, other hydrocarbons such as paraffins and also other organic material such as asphaltic compounds. The aromatic hydrocarbons may be isolated from the remaining organic matter by suitable chromatographic separation techniques. This may be accomplished by dissolvnig the extract in a suitable amount, e.g., five milliliters, of n-heptane and adding the resulting solution to a suitable chromatographic column. For example, the chromatographic column may be a ten millimeter diameter x 360 millimeter long glass column packed with nine grams of 100 to 200 mesh activated silica gel which is prewet with five milliliters of n-heptane. The chromatographic column then is eluted successively with two five-milliliter portions of heptane, three five-milliliter portions of carbon tetrachloride, three five-milliliter portions of benzene and three five-milliliter portions of methanol. The aromatic hydrocarbons in the extract will be recovered primarily in the benzene fraction of the column effluent although some aromatics also will be recovered in the methanol fraction. This latter fraction also will contain appreciable amounts of oxygenated compounds and it is therefore discarded.

The above-described chromatographic procedure usually will isolate the aromatic hydrocarbons from appreciable quantities of other organic compounds. However, in some instances the benzene fraction from the silica gel chromatography may include significant amounts of asphaltic compounds containing oxygen, nitrogen, and sulphur. When further treatment to insure the absence of significant quantities of such compounds is desired, the benzene fraction may be subjected to alumina chromatography. A suitable column for the alumina separation procedure may take the form of a ten milliliter diameter x 360 milliliter glass column packed with nine grams of alumina and prewet with five milliliters of n-heptane. In carrying out the alumina chromatography, the benzene fraction from the silica gel chromatography is subjected to evaporation in order to remove the solvent. The remaining residue then is dissolved in a five-milliliter portion of n-heptane and the resulting solution is added to the alumina column. The chromatographic column then is eluted successively with five milliliters of carbon tetrachloride and three five-milliliter portions of benzene. The fraction recovered from the column during the addition of the carbon tetrachloride and benzene contains aromatic hydrocarbons which are substantially free of any asphaltic compounds originally in the organic extract.

Following the chromatographic procedures, the aromatic hydrocarbon fraction is analyzed for the relative concentrations of primary hydrogen atoms associated with aromatic hydrocarbon structures having at least one primary hydrogen atom but not more than two such hydrogen atoms adjacent one another and the relative concentration of primary hydrogen atoms associated with aromatic hydrocarbon structures having four or five adjacent such hydrocarbon atoms. This may be accomplished by any suitable technique. For example, the conventional spectral methods such as infrared, ultraviolet, and nuclear magnetic resonance spectroscopy may be used. It has been found, however, in experimental work conducted regarding the invention that infrared spectroscopy is a relatively simple and yet highly accurate method for determining the structural distribution of the aromatic compounds and this technique is used in a preferred embodiment of the invention.

As noted previously, absorbance in the infrared spectrum in the region of 12.4 microns is a function of the abundance of primary hydrogen atoms on structures having one or two adjacent hydrogen atoms on an aromatic nucleus and absorbance in the region of 13.4 microns is a function of the abundance of primary hydrogen atoms on structures having four or five adjacent hydrogen atoms on an aromatic nucleus. Therefore, by measuring the infrared absorbance in these regions the structure distribution index may be determined as the ratio of maximum infrared absorbance in the region of 12.4 microns to maximum infrared absorbance in the region of 13.4 microns. It will be understood that by the qualification "in the region of" a designated wave length is meant the absorption band spanning this wave length. The absorption bands at 12.4 and 13.4 microns normally will extend about 0.3 or 0.4 microns on both sides of each of these points. The maximum absorbance for these absorption bands usually will be found at the respective wave lengths of 12.4 and 13.4 microns. However, some deviation from this may be experienced. For example, the maximum absorbance, i.e., minimum transmittance, for the 12.4 micron absorption band is sometimes found at about 12.3 microns. In any case, the absorption bands of interest will span 12.4 and 13.4 microns, respectively.

Preparatory to infrared analysis, the solvent is removed from the fraction recovered from the chromatographic column by a suitable drying procedure, such as by evaporation at 40° C. under air. The remaining residue then is dissolved in a solvent suitable for infrared spectroscopy. For example, the residue may be dissolved in spectral grade carbon disulfide in the amount of 10–20 milligrams of extract per milliliter of carbon disulfide. Infrared spectroscopy may be accomplished by the "cell-match" technique by means of a suitable double-beam recording spectrophotometer having two matched absorption cells. One cell is filled with spectral grade carbon disulfide for use as a reference beam and the other cell is filled with the sample dissolved in the carbon disulfide. The spectrophotometer is provided with suitable optics for the cells, e.g., silver chloride windows, suitable for scanning in the 12.4 micron and 13.4 micron regions. For example, the scanning may be carried out over the spectral interval of 12 to 14 microns. Usually however, it will be preferred to scan over a range of 10 to 15 microns. The results of the spectroscopic analysis may be recorded in accordance with standard practice in terms of percent transmittence as a function of wave length. percent transmittance is, of course, a functional representation of absorbance and thus the spectrogram provides a measure of the infrared absorbance in the regions of interest.

It will be recognized that the above-described analytical procedure is not determinative with regard to the absolute concentrations of primary hydrogen atoms associated with the two classes of aromatic hydrocarbon structures under consideration. The extraction technique does not recover all of the aromatic hydrocarbon content of the sample and also the above-described infrared spectroscopy technique yields results in terms of relative abundance of the primary hydrogen atoms. However, the procedure does give reliable results with regard to the relative concentrations of the primary hydrogen atoms associated with two classes of aromatic hydrocarbon structures and thus yields data from which the structure distribution index may be determined with accuracy.

A number of various procedures may be followed in practicing the present invention. For example, the invention may be utilized as a primary exploratory technique in order to determine the possibility of petroleum accumulations within a general geographical area of the earth's surface. In this case, it usually will be preferred to obtain samples from a relatively large number of locations in the earth's crust. The sampling stations may be chosen randomly or on the basis of a predetermined scheme and the samples may be obtained at the surface of the earth or by drilling to subsurface locations within the earth's crust.

The samples thus collected are analyzed by the above-described or other suitable analytical procedure to obtain for each sample the data necessary for the determination of the structure distribution index. The indices for the respective samples then are correlated with each other and the locations in the earth's crust at which the samples were taken in order to ascertain possible source rocks of petroleum hydrocarbons in the area. This may be accomplished by plotting the structure distribution index for each sample at its respective location on a geographical map of the area surveyed. If the results of this survey indicate that certain sediment formations within the earth's crust in the area under investigation may be source rocks, further exploratory measures then may be carried out.

The instant invention also may be utilized as a supplementary exploratory tool in areas within which other prospecting operations already have been carried out. For example, a seismic survey of a particular locality may indicate the presence of subsurface sedimentary structures favorable to the accumulation of petroleum hydrocarbons. In this case, the instant invention can provide a valuable tool in determining which one of these subsurface structures may actually contain such petroleum deposits.

In this use of the invention at least one, and preferably a plurality of, samples may be obtained from each of the source rock type formations in the area. Source rock type formations may be considered to be sediments such as shales and carbonate rocks, i.e., limestones and dolomites, which have a mineral matter content of not more than six percent and preferably not more than one percent by weight for carbonates, and a permeability of not more than one millidarcy. The samples then are analyzed for aromatic hydrocarbon structures from which the structure distribution index may be determined. The structure distribution indices then are correlated with each other and the rock formations from which the samples were obtained in order to ascertain a rock formation having a structure distribution index of more than 0.8. The location of this rock formation in the earth's crust then may be correlated with respect to the locations of the aforementioned possible reservoir formations and a well is drilled into a reservoir rock formation which is in fluid communication with the designated source rock formation and which has a permeability greater than the designated source rock formation. Preferably, the well is drilled into a reservoir rock formation, at least a portion of which is in a contiguous relationship with at least a portion of the source rock formation. By contiguous relationship is meant a reservoir rock formation which lies next to the source rock formation and thus provides a ready acceptor for petroleum hydrocarbons formed in the source rock and migrating therefrom. However, in some cases it may be desirable to drill a well into a promising reservoir rock formation which is not in a contiguous relationship with the source rock formation, but which is in fluid communication therewith by other means such as through subterranean faults or joints.

It is preferred in accordance with this invention to designate as source rocks only those rock formations having a structure distribution index of 0.8 or more. However, an exploratory survey carried out utilizing the instant invention may fail to reveal a source rock type sediment having a structure distribution index meeting the above criterion. In this case, if there is strong independent evidence of subsurface petroleum accumulations such as oil seeps, it may be desirable to designate the formation having the highest structure distribution index, even though it may be less than 0.8, as a petroleum source rock. Thus, in this situation, an exploratory well would be drilled into a subsurface rock formation which has suitable reservoir characteristics and is in fluid communication with the formation designated as a source rock. As stated before, the rock formation into which the well is drilled preferably will be in a contiguous relationship with the source rock. However, fluid communication between the source rock and reservoir rock formations may be established by other means such as through faulting.

In the above description, emphasis has been placed upon the application of the invention to carbonates. However, the invention may be utilized in the identification of shale source rocks, particularly where other methods such as the carbon preference index technique prove inconclusive.

Having described specific embodiments of the instant invention, it will be understood that further modifications thereof may be suggested to those skilled in the art, and it is intended to cover all such modifications as fall within the scope of the appended claims.

What is claimed is:

1. A method of geochemical exploration comprising: extracting organic matter from a sample obtained from an organic matter containing formation in the earth's crust, isolating aromatic hydrocarbons having at least ten carbon atoms from said extracted organic matter, and subjecting said isolated aromatic hydrocarbons to infrared spectrometry in the regions of 12.4 microns and 13.4 microns and measuring the maximum infrared absorbance in each of said regions, the maximum infrared absorbance in the region of 12.4 microns being a function of the relative concentration of primary hydrogen atoms on aromatic hydrocarbon structures having at least one primary hydrogen atom and not more than two primary hydrogen atoms adjacent and the maximum infrared absorbance in the region of 13.4 microns being a function of the relative concentration of primary hydrogen atoms on aromatic hydrocarbon structures having at least four adjacent primary hydrogen atoms and not more than five adjacent primary hydrogen atoms.

2. The method of claim 1 wherein the aromatic hydrocarbons isolated from said organic matter have at least 18 carbon atoms.

3. The method of claim **1** wherein said sample is from a formation having an organic matter content of not more than six percent by weight.

4. The method of claim **1** wherein said sample is from a carbonate formation having an organic matter content of not more than one percent by weight and a permeability of not more than one millidarcy.

5. The method of claim **1** wherein the ratio of maximum infrared absorbance in the region of 12.4 microns to maximum infrared absorbance in the region of 13.4 microns is at least 0.8, further comprising the step of drilling a well into a subsurface reservoir formation in fluid communication with said first named formation, said reservoir formation having a permeability greater than said first named formation.

6. The method of claim **5** wherein at least a portion of said reservoir formation is in a contiguous relationship with at least a portion of said first named formation.

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