

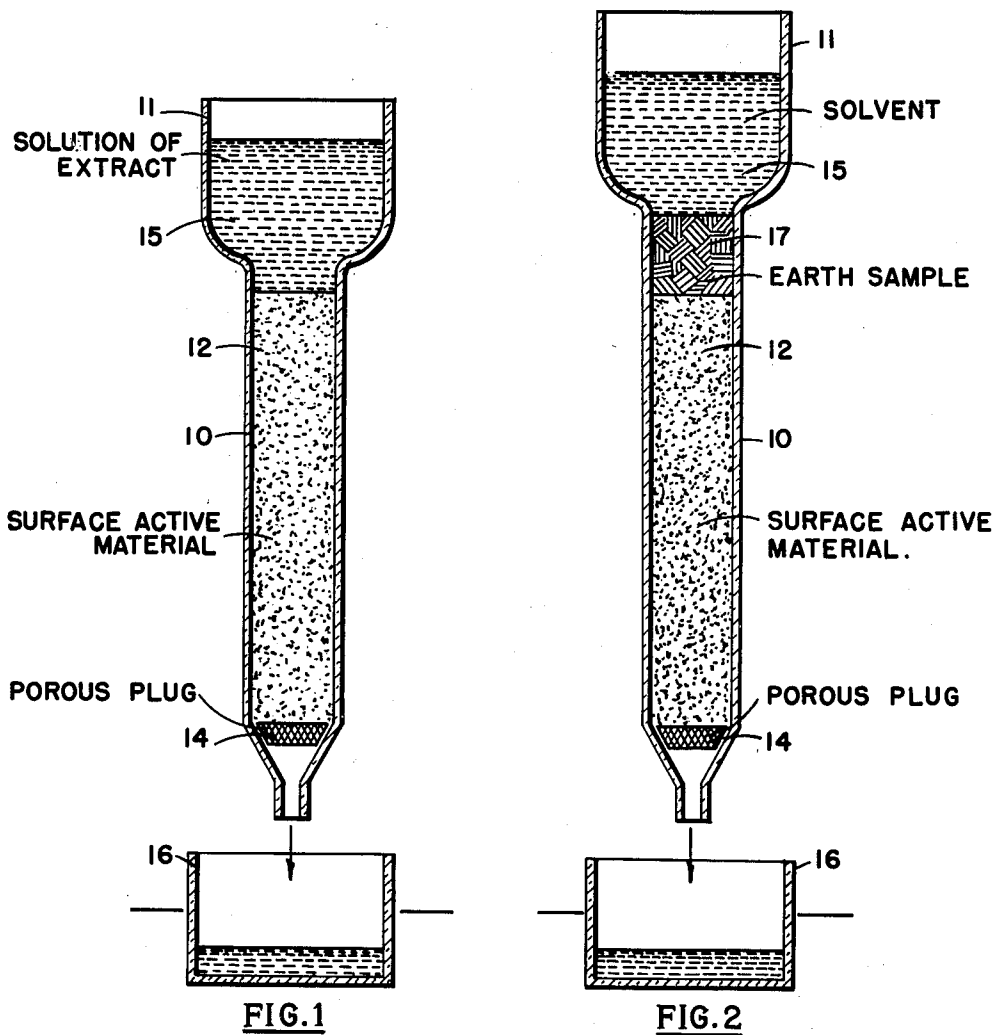
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METHOD OF ANALYZING EARTH MATERIALS FOR HYDROCARBONS

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METHOD OF ANALYZING EARTH MATERIALS FOR HYDROCARBONS

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This invention relates to geochemical exploration and relates more particularly to the analysis of earth samples for paraffin hydrocarbons as an aid in the location of petroleum hydrocarbon reservoirs.

In exploration for underground petroleum hydrocarbon reservoirs, either of gas or oil, extensive use has been made of geochemical methods. These methods are based upon the theory that hydrocarbons migrate upwardly from the underground reservoir and their presence, or the presence of their decomposition or reaction products, in the surface or near surface zones or in the strata intermediate to the near surface zones in quantity greater than the background quantity, i. e., as an anomaly, is indicative of the location of the underlying reservoir. Thus as a prospecting method or a well logging method, samples of earth material have been collected and analyzed for various paraffin hydrocarbons or groups of paraffin hydrocarbons, anomalies of which are regarded as diagnostic of an underground petroleum reservoir. However, the paraffin hydrocarbons are in extremely small quantity in most earth samples and their separation for quantitative determination from other compounds and hydrocarbons other than paraffins which are present in the earth samples have not been possible with accuracy and precision.

It is an object of this invention to provide a geochemical exploration method. It is another object of this invention to provide a geochemical prospecting and well logging method. It is another object of this invention to provide a method for the analysis of earth samples. It is another object of this invention to provide a method for analyzing earth samples for paraffin hydrocarbons significant with respect to the proximity of a petroleum hydrocarbon reservoir. It is another object of this invention to provide a simple and rapid procedure for separating a desired paraffin hydrocarbon portion, significant with respect to the proximity of a petroleum hydrocarbon reservoir, from other components of an earth sample. It is another object of this invention to provide a simple and rapid procedure for separation of hydrocarbons from earth samples to determine diagnostic anomalies. Further objects of the invention will become apparent from the following description thereof.

In accordance with the invention, as a first step, an earth sample is treated to obtain an extract dissolved in a solvent for paraffin hydrocarbons, which solvent has a greater affinity for being adsorbed on surfaces than the paraffin hydrocarbons desired to be separated from the other constituents of the earth sample but a lesser affinity for being adsorbed on surfaces than these other constituents of the soil sample contained in the extract. As a second step, the solution of extract is subjected to adsorption-fractionation whereby a solution is obtained containing only the paraffin hydrocarbons desired to be separated from the other constituents of the earth sample. The quantity or identity of paraffin hydrocarbons in the solution is then determined by suitable means. By this process, the paraffin hydrocarbons desired are simply

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and rapidly separated from the other constituents of the earth sample and their identification or quantitative estimation may be made without interference by the other constituents of the sample.

Figure 1 schematically illustrates a method and apparatus for carrying out the adsorption-fractionation step.

Figure 2 schematically illustrates a method of extracting the earth sample and carrying out the adsorption-fractionation step as one operation.

Adsorption-fractionation comprises passing the solution of extract containing the paraffin hydrocarbons and other constituents of the earth sample through a body, such as a column, of surface active material. By surface active material is meant any material which has a high surface area per volume of material. These materials are well known in the art of chromatography, and include silica gel, alumina gel, clay, fuller's earth, and other highly adsorbent materials. The more adsorbable constituents in the solution of extract are adsorbed first on the surface active material and, as the solution of extract percolates through the surface active material, the less adsorbable materials are progressively adsorbed. Each constituent of the solution of extract including each paraffin hydrocarbon has a characteristic adsorbability, but, as will be pointed out in greater detail hereinafter, each paraffin hydrocarbon is less adsorbable than any non-paraffin hydrocarbon constituent of the earth sample contained in the extract. Thus, where the surface active material is employed in an amount sufficient to absorb a part of the solvent, and the solvent is the constituent in greatest volume in the solution of extract, the solution leaving the surface active material will contain the paraffin hydrocarbon portion of the earth sample less adsorbable than the solvent and will be free of any constituent of the earth sample more adsorbable than the solvent. By selection of the solvent, part or all of the paraffin hydrocarbons may be the only or the predominating constituent, as desired, of the earth sample remaining in the solvent after adsorption-fractionation. The solvent must be the constituent in greatest volume in the solution of extract, for example, ten times as great in volume as the total volume of the other constituents. Greater volumes of solvent, however, are preferred to insure complete separation.

Following adsorption-fractionation, the quantitative determination of the paraffin hydrocarbons may be made by any suitable procedure. Suitable procedures include removal, as by evaporation, of the solvent from the solution obtained from the adsorption-fractionation step, and weighing of the residue, the entire residue being regarded as paraffin hydrocarbon. In this connection, if evaporation is employed, the evaporation should be carried out at such temperatures and under such conditions that paraffin hydrocarbons having a boiling point higher than the solvent will not be evaporated along with the solvent unless it is desired to remove some of the lighter paraffin hydrocarbons. Another procedure involves measuring the absorption of infrared radiation, such as in the 3 to 4 micron region, by the solution obtained by adsorption-fractionation. Where this latter procedure is employed, the solvent must be one which is transparent to the infrared radiation in the region employed but, if not, the solvent may be removed by evaporation and the residue dissolved in a solvent transparent to the infrared radiation in the region employed. Another method for quantitatively determining paraffin hydrocarbons is mass spectroscopy which has the advantage of distinguishing a paraffin hydrocarbon solvent from other paraffin hydrocarbons obtained from the earth sample.

The paraffin hydrocarbons contained in an earth sample as a result of migration from a petroleum reservoir

constitute methane and those paraffin hydrocarbons having a greater number of carbon atoms, for example, up to sixteen carbon atoms or more. Thus, anomalies of a single paraffin hydrocarbon, groups of paraffin hydrocarbons, or all of the paraffin hydrocarbons in earth samples are diagnostic of the proximity of a petroleum hydrocarbon reservoir. Depending upon the solvent employed, the process of the invention may be carried out so that groups or all of the paraffin hydrocarbons significant with respect to the proximity of a petroleum hydrocarbon reservoir may be contained in the solution after adsorption-fractionation. While methane may be present in the earth samples as a result of migration from a petroleum reservoir, it may also be present as a result of other causes, such as vegetative decomposition, and, for this reason, methane should be excluded from the paraffin hydrocarbons for which analysis is made if its presence could be due to causes other than migration from a petroleum reservoir.

The relative order of adsorbability on surface active material, such as silica gel, of the classes of organic compounds ordinarily found in the earth samples and the ordinary classes of organic solvents in which paraffin hydrocarbons are soluble is as follows:

1. Heavy isoparaffin hydrocarbons.
2. Light isoparaffin hydrocarbons.
3. Heavy normal paraffin hydrocarbons.
4. Light normal paraffin hydrocarbons.
5. Monocyclic hydrocarbons and halogenated carbon compounds.
6. Aromatic hydrocarbons and saturated polycyclic hydrocarbons.
7. Oxygenated compounds.

In the above tabulation, the classes of compounds are listed in order of increasing adsorbability, i.e., the heavy isoparaffins are less capable of being adsorbed on surface active material than the light isoparaffins, the light isoparaffins are less capable of being adsorbed than the heavy normal paraffins, etc.

The selection of the solvent for preparing the solution of extract to be passed through the body of surface active material may be made in accordance with above tabulation. Thus, if anomalies of heavy isoparaffins as a group in the earth samples are being taken as diagnostic of a petroleum reservoir, a light isoparaffin solvent may be employed as the solvent for the extract during adsorption-fractionation. If anomalies of the heavy and light isoparaffins and the heavy normal paraffins as a group are taken as diagnostic of a petroleum hydrocarbon reservoir, a light normal paraffin may be employed as the solvent. Similarly, selection of the solvent may be made where anomalies of other paraffin hydrocarbons are taken as diagnostic of a petroleum hydrocarbon reservoir. For each solvent, those compounds preceding it in the above tabulation, and, where the solvent is a paraffin hydrocarbon, the heavier paraffin hydrocarbons within the same class, will be retained in the solution following adsorption-fractionation.

Generally, it is desirable to employ a solvent which is liquid at ordinary conditions of temperature and pressure. However, solvents which are solid or gaseous at ordinary conditions of temperature and pressure may be employed by maintaining proper conditions of temperature or pressure or both to keep the solvent in the liquid phase. Paraffin and isoparaffin solvents which may be employed for adsorption-fractionation include ethane, propane, normal butane, isobutane, normal pentane, isomeric pentanes, normal hexane, isomeric hexanes, normal heptane, isomeric heptanes, etc. Of these, normal pentane and normal heptane are preferred since each can retain, during adsorption-fractionation, all but a few of the light normal paraffins that may have been contained in the solution, each remains in the liquid state at ordinary temperatures and pressures, and when

each is to be removed by evaporation, only a few of the light normal paraffins that may have been contained in the solution will be removed along with the solvent.

Where anomalies of all the paraffin hydrocarbons, as a group, are to be taken as diagnostic of a petroleum reservoir, a halogenated carbon compound may be employed as solvent. With such solvents, of course, any naphthenes that may have been contained in the earth sample can be present in the solution after adsorption-fractionation. However, the amount of the naphthenes may be small as compared to the amount of the paraffin hydrocarbons and therefore, can be neglected. Suitable halogenated solvents include carbon tetrachloride, carbon tetrabromide, carbon tetraiodide, and carbon tetrafluoride. These compounds have the advantage that quantitative determination of the paraffin hydrocarbons can be made following adsorption-fractionation by infrared absorption methods without necessity for removal of solvent by evaporation. Of the halogenated solvents, carbon tetrachloride is preferred because of availability, economy, and the fact that it is highly efficient as a solvent for extracting the earth sample.

Solvents other than those mentioned hereinbefore may be used and their suitability for use may be determined from knowledge of their adsorbabilities. The adsorbability of any solvent relative to earth sample constituents may be ascertained by dissolving the earth sample constituent in the solvent, passing the solution through a body of surface active material, and analyzing the resulting liquid to determine whether the solvent or the earth sample constituent is preferentially adsorbed.

In the practice of the invention, earth samples are collected and then extracted with a solvent in the conventional manner. The samples may be extracted in a Soxhlet extractor or may be subjected to batch extraction. The earth sample should be sufficiently large to obtain a measurable quantity of hydrocarbons in the extract solution and sufficient solvent should be used to obtain a volume of solution which is readily handled. For example, the earth sample may weigh about 150 grams and sufficient solvent may be employed to obtain about 50 milliliters of extract solution. The solvent to be employed for extraction may be any solvent in which paraffin hydrocarbons are soluble and may be any of the organic solvents heretofore employed in the geochemical art for the extraction of earth samples. Suitable solvents include those hereinabove mentioned as being suitable for adsorption-fractionation as well as chloroform, bromoform, carbon disulfide, petroleum ether, acetone, methanol, ethanol, propanol, di-ethyl ether, etc. Mixtures of solvents may be employed, such as an equimolar mixture of an alcohol and carbon tetrachloride.

The solvent employed for extraction of the sample may be the same solvent to be employed in the adsorption-fractionation step, or may be a different solvent. Where a different solvent is employed, all the solvent is removed by evaporation from the solution obtained by extraction and the residue is dissolved in the solvent to be employed for adsorption-fractionation. In this connection, where removal of the solvent by evaporation from the solution obtained by extraction or by adsorption-fractionation is required, the evaporation procedure may remove some of the paraffin hydrocarbons obtained from the earth sample. This will occur, for example, where the solvent has a higher boiling point than some of the paraffin hydrocarbons. Accordingly, selection of the solvent to be employed for extraction or for adsorption-fractionation must be made taking into consideration, in the light of the particular paraffin hydrocarbons which are being regarded as significant with respect to the proximity of a petroleum hydrocarbon reservoir and for which analysis of the earth sample is being made, the necessity of a subsequent evaporation procedure.

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A method and apparatus for carrying out the adsorption-fractionation step is illustrated in Figure 1. Referring to Figure 1, a tube 10, which may be of any suitable material such as glass, and having an upper wide mouth portion 11, is filled at its lower portion with a column of surface active material 12. A porous plug 14, permeable to liquid, is positioned at the bottom portion of the tube to maintain the column of surface active material within the tube. The solution of extract 15 is placed within the wide mouth portion 11 of the tube and percolates downwardly through the column of surface active material to receiving vessel 16. Thereafter, a portion of the solvent employed for preparing the solution of extract 15 is passed through the column as washings and added to the solution of extract in receiving vessel 16.

The column of surface active material 12 should be of sufficient volume to adsorb all the components of the earth sample more adsorbable than the solvent but, as previously mentioned, insufficient to adsorb all of the solvent. Preferably, the column of surface active material should be of such volume that only a small portion of the solvent is adsorbed. Satisfactory results have been obtained with columns of surface active material 10 centimeters in length and 1 centimeter in diameter where the volume of the extract solution is about 50 milliliters. Conveniently, the column of surface active material may be mounted vertically as shown in Figure 1 and the extract solution passed through by means of gravity, although the column may be mounted horizontally and the extract solution passed through by pressure.

Extraction of the earth sample and adsorption-fractionation of the extract solution may be effected, if desired, in one operation. A method of carrying out this procedure is illustrated in Figure 2. The column of surface active material 12 is positioned within the tube 10 above the porous plug 14 and the earth sample 17 is placed above the surface active material. The solvent, which in this case must be the solvent desired for use in adsorption-fractionation, is placed within the wide mouth portion 11 of the tube and the solvent percolates downwardly through the tube resulting in extraction of the earth sample 17 and adsorption-fractionation of the extract solution. Following adsorption-fractionation, the extract solution and the washings are analyzed for the paraffin hydrocarbons contained therein.

Herein, by "extract" I mean that portion of the earth sample, either prior or subsequent to adsorption-fractionation, which has been removed from the earth sample by extraction of the earth sample with a solvent, and which may or may not be in solution. By "solution of extract" or "extract solution" I mean the extract in solution in a solvent, whether the solvent is one employed for extracting the earth sample, for carrying out adsorption-fractionation, or one in which quantitative determination of paraffin hydrocarbons, as by infrared adsorption, is made. By "residue," I mean the extract as obtained by evaporation of its solution in any solvent. By "paraffins," I mean both normal paraffins and isoparaffins.

The process of the invention may be employed in geochemical exploration including prospecting and well logging. In geochemical prospecting, earth samples may be taken at surface or near surface points along a traverse or otherwise and the concentration of paraffin hydrocarbons determined to detect anomalies indicative of an underlying reservoir of oil or gas. In geochemical well logging, samples, such as cores, may be taken of the strata along the path of the well, and their paraffin hydrocarbon concentrations determined as indicative of the proximity of a producing strata.

The sensitivity of the process of the invention is high, analysis of earth samples containing as low as 0.5 microgram of paraffin hydrocarbons per gram of earth having been made with an error of only 0.13 microgram.

The following will be further illustrative of the inven-

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tion. Surface soil samples were collected at 80 points located above a known oil pool and at 80 points located at a distance around the oil pool. Each sample which weighed about 150 grams was extracted in a Soxhlet extractor with carbon tetrachloride to obtain about 100 milliliters of extract solution from each sample. The carbon tetrachloride solvent was removed from the extract solutions by evaporation at 40° C. using a stream of air to assist in evaporation. Approximately 10 milliliters of normal heptane, which had been purified of more adsorbable hydrocarbons by passing through a column of silica gel and then distilled, were added to each residue. The resulting solution was then passed through a column of silica gel 10 centimeters in length and 1 centimeter in diameter. The silica gel was 200 mesh in size and had been activated by heating at 425° C. for 6 hours. Another 10 milliliters of purified normal heptane were added to the residue and the resulting solution passed through the column of silica gel after the level of the first 10 milliliters had passed the top of the column. The process was repeated until the entire amount of the residue soluble in the normal heptane was dissolved. The normal heptane was removed from the solution by evaporation at about 40° C. with the aid of a stream of air and the residue was dissolved in about 25 milliliters of carbon tetrachloride. The concentration of paraffin hydrocarbons in the carbon tetrachloride solution was then determined by measuring the extent to which the solution absorbed infrared radiation in the 3 to 4 micron region. The average concentration of paraffin hydrocarbons in the soil samples taken at points above the oil pool was 1.04 micrograms per gram of soil whereas the average concentration of paraffin hydrocarbons in the soil samples taken at points around the oil pool was 0.76 microgram per gram of soil. It will be apparent that, by the process of invention, an anomaly indicative of the location of the oil pool was obtained.

Having thus described my invention, it will be understood that such description has been given by way of illustration and example only and not by way of limitation, reference for the latter purpose being had to the appended claims.

I claim:

1. In a geochemical exploration method wherein earth samples are collected from an exploration zone and analyzed for a desired paraffin hydrocarbon portion, anomalies of which are significant with respect to the proximity of an underground petroleum hydrocarbon reservoir, the steps which comprise collecting earth samples from an exploration zone, extracting each of said earth samples with a solvent in which paraffin hydrocarbons are soluble to obtain an extract of each of said earth samples, passing each of said extracts through solid surface active material while said extracts are in solution in at least ten times their volume of a solvent which is more adsorbable on said surface active material than a desired paraffin hydrocarbon portion of the constituents of said earth samples contained in said extracts but less adsorbable on said surface active material than the other constituents of said earth samples contained in said extracts whereby said desired paraffin hydrocarbon portions of the constituents of said earth samples are separated from the other constituents of said earth samples by adsorption on said surface active material of the other constituents of said earth samples, recovering each of said solutions containing said desired paraffin hydrocarbon portions of the constituents of said earth samples passed through said surface active material, and analyzing each of said solutions for said desired paraffin hydrocarbon portions of the constituents of said earth samples.

2. In a geochemical exploration method wherein earth samples are collected from an exploration zone and analyzed for a desired paraffin hydrocarbon portion, anomalies of which are significant with respect to the proximity of an underground petroleum hydrocarbon reservoir, the

5. In a geochemical exploration method wherein earth samples are collected from an exploration zone and analyzed for a paraffin hydrocarbon portion, anomalies of which are significant with respect to the proximity of an underground petroleum hydrocarbon reservoir, the steps which comprise collecting earth samples from an exploration zone, extracting each of said earth samples with a solvent in which paraffin hydro-

8. In a geochemical exploration method wherein earth samples are collected from an exploration zone and analyzed for a paraffin hydrocarbon portion, anomalies of which are significant with respect to the proximity of an underground petroleum hydrocarbon reservoir, the steps which comprise collecting earth samples from an exploration zone are:

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the constituents of said earth samples passed through said surface active material, and analyzing each of said solutions for said paraffin hydrocarbon portions of the constituents of said earth samples.

15. In a geochemical exploration method wherein earth samples are collected from an exploration zone and analyzed for a desired paraffin hydrocarbon portion, anomalies of which are significant with respect to the proximity of an underground petroleum hydrocarbon reservoir, the steps which comprise collecting earth samples from an exploration zone, passing through each of said earth samples a solvent in which paraffin hydrocarbons are soluble and which is more adsorbable on solid surface active material than a desired paraffin hydrocarbon portion of the constituents of said earth samples but less adsorbable on surface active material than the other constituents of said earth samples soluble in said solvent, the volume of solvent being at least ten times as great as the volume of material extracted from said earth sample, passing each of the resulting solutions leaving said earth sample through surface active material whereby a desired paraffin hydrocarbon portion of the constituents of said earth samples is separated from the other constituents of said earth samples by adsorption on said surface active material of the other constituents of said earth samples, recovering each of said solutions containing said desired paraffin hydrocarbon portions of the constituents of each of said earth samples passed through said surface active

material, and analyzing each of said solutions for said desired paraffin hydrocarbon portion of the constituents of said earth samples.

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