

June 26, 1945.

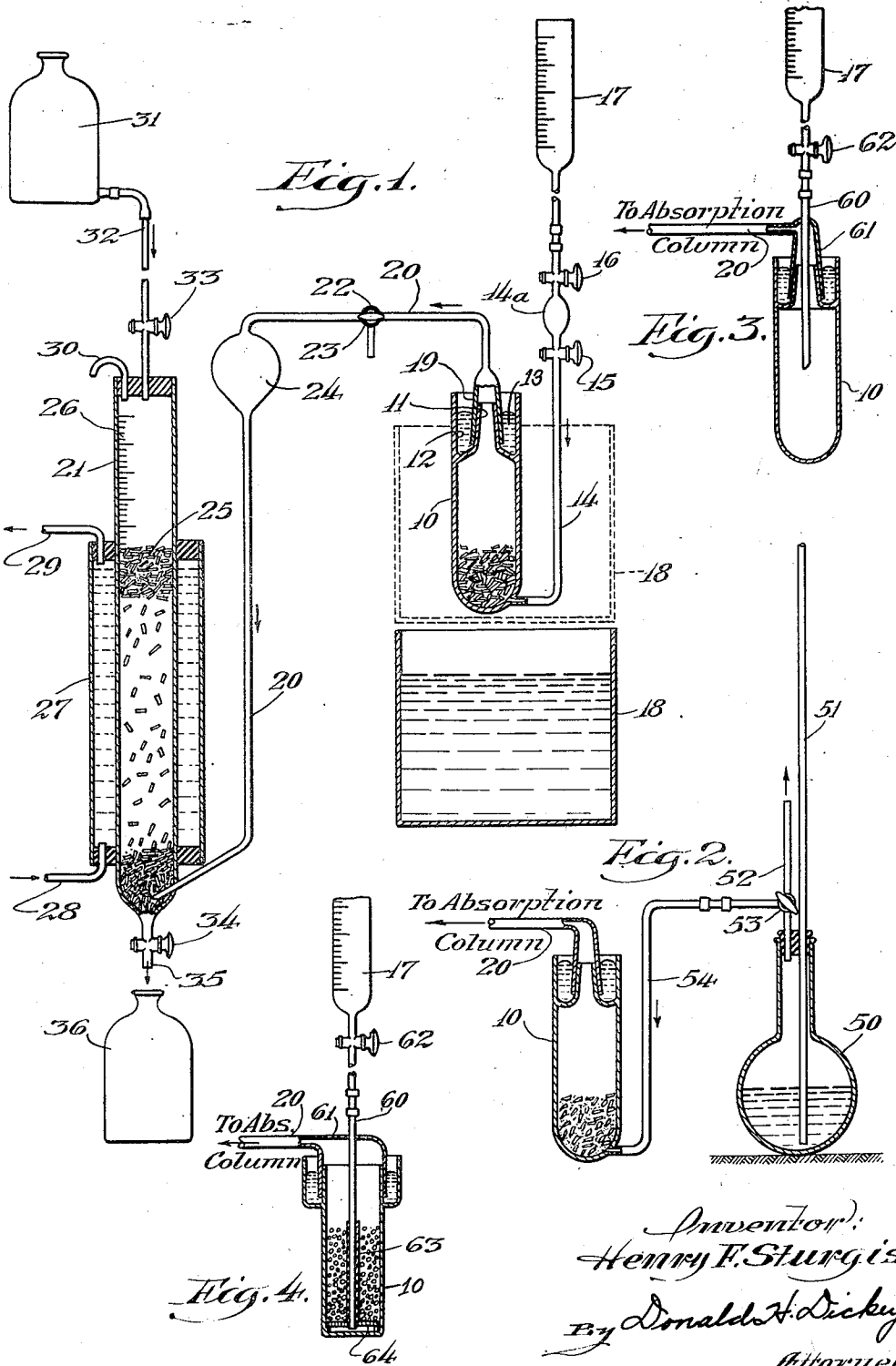
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ANALYZING EARTH FORMATIONS

Filed May 29, 1941

2 Sheets-Sheet 1



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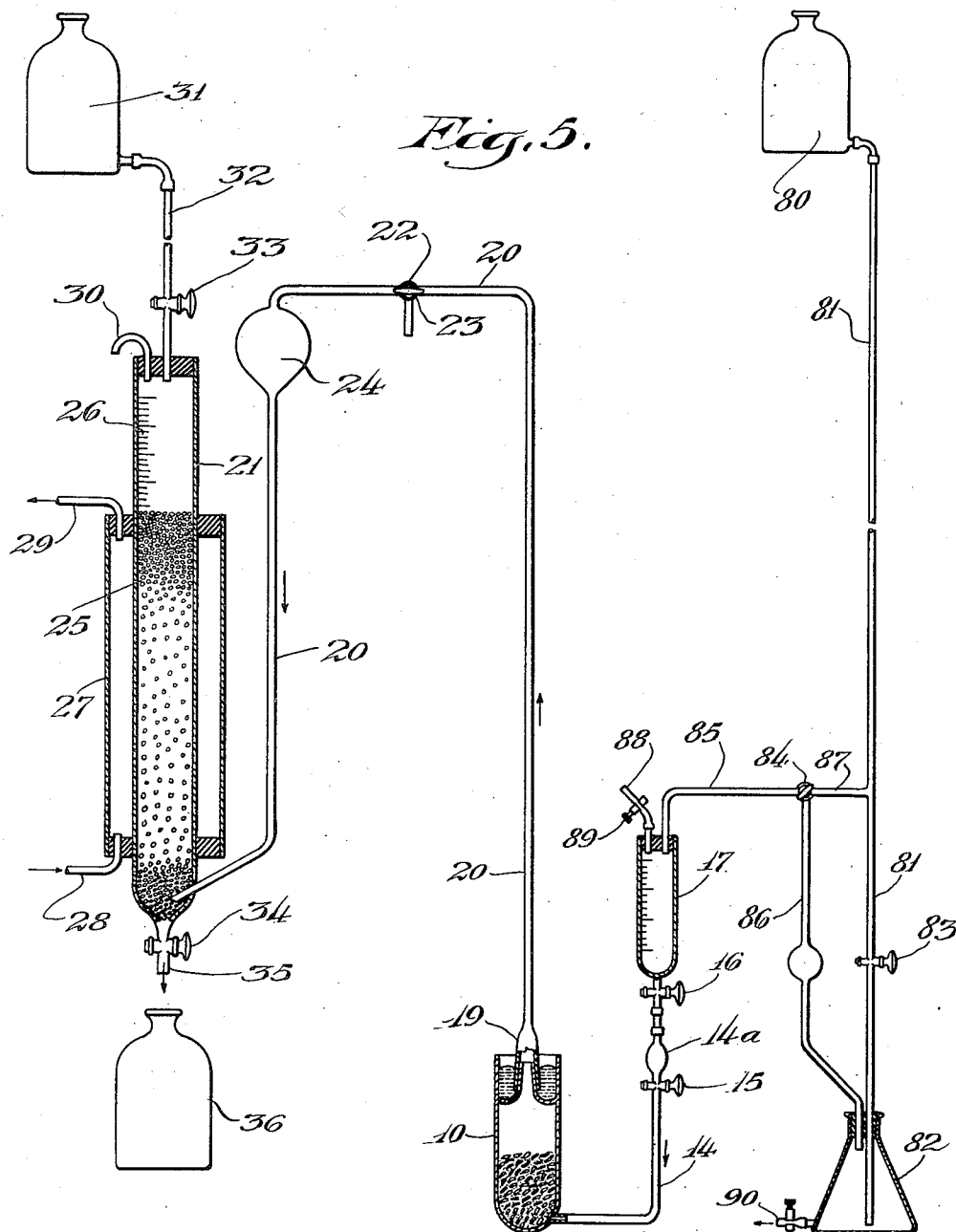
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Inventor:
Henry F. Sturgis
By Donald H. Dickey
Attorney.

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ANALYZING EARTH FORMATIONS

Henry F. Sturgis, Tulsa, Okla., assignor to Stan-
olind Oil and Gas Company, Tulsa, Okla., a
corporation of Delaware

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9 Claims. (Cl. 73-153)

This invention relates to the analysis of earth formations and particularly to geochemical prospecting and especially to geochemical well logging. This invention is particularly concerned with the determination of the hydrocarbon and water content of drill cuttings from subsurface formations.

It has been found that the presence of various hydrocarbons or quasi-hydrocarbons in drill cuttings from subsurface formations or from surface soils is related to the presence of oil and gas deposits located in deeper strata far below. These hydrocarbons and quasi-hydrocarbons which serve as indicia of the petroleum deposits include gaseous, liquid and solid materials. The hydrocarbon content of samples of drill cuttings or surface soils is determined by analysis, these determinations being used in preparing a log or map to obtain an indication of the presence and location of oil and gas deposits.

In making a geochemical well log, samples of the drill cuttings are taken at frequent vertically spaced intervals along a well bore, and the samples analyzed by any of various methods for various hydrocarbon or quasi-hydrocarbon constituents, and the results for the various samples are compared and plotted in order to obtain a log of the well which indicates the presence and location of oil and gas deposits in the deeper strata.

It is an object of my invention to provide a new and improved method and means for the recovery of hydrocarbons from drill cuttings. Another and more detailed object is to provide an improved method and means for separating hydrocarbons from wet drill cuttings for geochemical well logging. A further object of my invention is to provide an improved method and means for determination of water in a wet sample of drill cuttings while recovering hydrocarbons therefrom, allowing all geochemical values to be reduced to a "dry sample" basis for comparison.

A still further object of my invention is to provide a new method and means whereby a larger percentage of the hydrocarbons present in drill cuttings, cores, surface soils, or other earth formations, can be recovered than has heretofore been possible. An additional advantage of my invention is the minimization of solvent evaporation during the absorption of hydrocarbons obtained from drill cuttings, cores, surface soils, and other earth formations. Other objects and advantages will become apparent as the description of my invention proceeds.

In the drawings:

Figure 1 is an elevation, partly in section, of one form of apparatus suitable for use in accordance with my invention; and

Figures 2, 3, 4, and 5 illustrate in elevation, partly in section, various forms of retorts and steam generators suitable for use with the absorption apparatus shown in Figure 1.

My invention will be described with particular reference to the analysis of samples of drill cuttings but it should be understood that it is also applicable to the analysis of samples of surface soils taken from horizontally spaced survey stations in the course of a geochemical prospecting operation and it is likewise applicable to the analysis of cores taken from wells, including cores taken from oil and gas bearing strata and to the analysis of other earth formations to determine hydrocarbons, water, or both.

Samples of drill cuttings or cores taken at selected spaced vertical points along a well bore can be transferred to sample jars which are tightly closed or sealed to prevent any evaporation loss. Heretofore it has usually been considered necessary or desirable to "air dry" the samples under more or less controlled conditions in order to obtain comparable values on a "dry basis." Naturally under such conditions greater or lesser amounts of hydrocarbons are apt to be lost by evaporation, and although comparative values between samples from various points might still be indicative of the relative amount of oil or gas present in the formation, evaporation losses are apt to vary widely, so that a truly comparative value cannot be obtained. Determination of the actual amount of hydrocarbons present in the sample will supply much more accurate information relative to the hydrocarbon content of the deeper strata of earth formation. Also, the "air dried" samples are usually crushed to a grain size, which increases the loss of hydrocarbons by evaporation due to the additional surface exposed by the crushing.

According to my invention, a portion of the wet drill cuttings or core is weighed directly from the sample bottle into a retort without intermediate air drying or crushing. The hydrocarbons and water are then driven off by externally applied heat from a constant temperature bath, and the released hydrocarbons and water bubbled through a solvent or absorbent which absorbs the hydrocarbons and condenses the water. To insure complete removal of the hydrocarbons from the sample, provisions are made to flush them from the sample and apparatus with steam.

The solvent with the hydrocarbons therein can

then be separated from the water and condensed steam, and the hydrocarbon constituents ascertained by any one of a number of methods as, for example, by the refractive index method described in U. S. Patent No. 2,213,905 to Clark or the density method set forth in the co-pending application of Thompson Serial Number 336,411.

These particular methods of determining hydrocarbons from samples of earth formations are especially applicable in conjunction with the present invention, since they require no separation of the absorbed hydrocarbons from the solvent. In the Clark method, a solvent of known refractive index is used to absorb the hydrocarbons, the solvent being chosen with a refractive index substantially different from that of the hydrocarbons found in the samples. By comparing the refractive index of a standard volume of extracted hydrocarbon and solvent with similar solvent hydrocarbon mixtures from samples taken at other points, variations in hydrocarbon content can be easily plotted. On the other hand, if the quantity and nature of the absorbed hydrocarbons is of particular interest, this can be determined from the solvent-hydrocarbon mixture by optical titration, using another solvent having a radically different refractive index. The Thompson method of determining hydrocarbons from samples of earth formations is based on variations in relative density, the solvent being of known density and the deviation therefrom caused by the presence of the absorbed hydrocarbons being a measure of the hydrocarbon content and the nature thereof.

Other methods of analysis include separation of the hydrocarbons from the solvent, and their measurement, with or without determination of their make-up, e. g. by fractional distillation using liquid air; combustion analysis; Raman spectra; infrared spectra; mass spectra; or other methods known to the art. These, however, while included within the scope of this application, require considerably greater technique in separating the hydrocarbons from the solvent without loss of various constituents.

Referring now to Figure 1, sample retort 10 is fitted with a male joint 11 within shoulders 12 adapted to hold a mercury seal 13. From one side of the base of retort 10 there extends a water delivery tube 14 equipped with stock cocks 15 and 16 with a reservoir 14a therebetween and surmounted by a graduated measuring cylinder 17. A thermostatically controlled bath 18 is supplied to surround and heat the lower part of retort 10 containing the sample. The lower portion of water delivery tube 14 is also encompassed by the bath 18 when the bath is in the elevated position shown in dotted lines.

Male joint 11 on retort 10 fits into the female joint 19 of delivery tube 20 which extends from retort 10 to the base of absorption column 21. Delivery tube 20 is also equipped, if desired, with a T 22 having a three-way stopcock 23 therein, and a solvent trap 24, trap 24 being at a height sufficient to prevent the overflow of solvent from absorption cylinder 21 to retort 10.

Absorption cylinder 21 can be filled throughout the lower portion of its length with packing material 25 which can consist of small lengths of glass rod or glass tubing, ceramic material, broken quartz, etc., or baffles or other means can be used, which will impede the upflow of materials entering from line 20 and cause increased contact between the absorption medium and the gaseous materials. The upper part of absorption column

21 is provided with markings 26 to indicate the volume. Column 21 is also surrounded by a water jacket 27 throughout the greater part of its length, water or other cooling medium entering through line 28 and discharging through line 29. By this means, the hot products from line 20 are cooled and condensed as well as absorbed in the absorption medium and the escape of any considerable quantity of liquefiable material is thereby prevented. An escape line 30 is provided for uncondensed gases. An absorption medium, which can suitably be carbon tetrachloride, carbon disulfide, dibromoethane, tetrabromoethane, benzene, cyclohexane, normal pentane, light naphtha, etc., is provided from a source 31 through line 32 leading to column 21, line 32 being provided with a stopcock 33. Absorption medium containing absorbed material, as well as condensed water and steam, can be withdrawn from column 21 by opening stopcock 34 in line 35, the liquid being collected in a container 36.

In operation a weighed amount of drill cutting sample is placed in retort 10 and constant temperature bath 18 elevated to surround the major portion of the retort as well as line 14 from measuring cylinder 17. Stopcocks 15 and 16 are closed and stopcock 22 turned to form a single passage from retort 10 to absorption column 21. Sufficient absorption medium, for example carbon tetrachloride, is added to column 21 by opening stopcock 33 (stopcock 34 being closed) to fill column 21 at least as high as the markings 26. The temperature of the constant-temperature bath is regulated to provide temperatures up to 600° F. or higher, although temperatures of from about 550 to about 600° F. will effectively remove all of the moisture and most of the hydrocarbons from the sample. Temperatures as low as about 250° F. are acceptable, however, since the steam will flush out all of the hydrocarbons from the sample at this temperature. When substantially all of the moisture and hydrocarbons, as well as any other volatile materials, have been removed from the sample, a measured amount of water is admitted from measuring cylinder 17 by opening valve 16 which permits reservoir 14a to be filled. This substantially total removal of hydrocarbons is determined for any group of samples by heating one sample for varying lengths of time to a fixed temperature, and measuring the relative completeness of the desorption process with time. Then all samples are heated for the length of time found to give substantially complete desorption. Typically this time is about one half hour at 550° F. By closing valve 16 and opening valve 15, water from reservoir 14a will flow through line 14 in heated bath 18 to retort 10. As the water passes in the tube through the hot bath to retort 10 it is converted into steam which rises through the sample in retort 10, sweeping out the hydrocarbon vapors through the retort and tubing into the absorption column.

Since the water both from the sample and from the condensed steam will be collected above the carbon tetrachloride in column 21, and since the amount of water converted to steam can be ascertained from measuring cylinder 17, it is a simple matter to subtract the amount of water collected above the carbon tetrachloride from the amount added from measuring cylinder 17 to determine the amount of water originally in the sample. This particular arrangement also has an added advantage that the water which collects above the carbon tetrachloride column acts as a seal, thus reducing any carbon tetrachloride evapora-

tion losses which might carry with them minor amounts of hydrocarbons.

After the hydrocarbons and contained water from the sample have been flushed with steam, stopcock 22 can be so regulated as to cut off the passageway in line 20 from retort 10 to absorption column 21, and the carbon tetrachloride with its absorbed hydrocarbons can be withdrawn by opening stopcock 34 in line 35. The enriched absorption medium is collected in vessel 36 from which samples can be obtained for hydrocarbon analyses by any of the previously mentioned means. From the weight of the sample and the amount of moisture determined therein, it is possible to determine the percentage of hydrocarbons present in the wet drill cuttings on a "dry basis," or if desired, on dried samples, since such samples can be analyzed equally well by my method.

Several variations in retort construction are suitable for carrying out my process, depending to a large extent upon the particular information desired. For example, Figure 2 illustrates the use of a separate steam generator as an external unit. A flask or other medium 50 is partially filled with water and is tightly stoppered, the stopper being provided with a safety tube 51 and an outlet 52 in which is a three-way stopcock 53 leading both to the outlet tube 52 and a tube 54 leading to retort 10. Heating means (not shown) are provided to vaporize the water in flask 50. With this arrangement the steam is injected into the retort under considerable pressure, since the generator is kept under a constant head of steam through the use of safety tube 51. Excessive pressure can be released by exhausting the steam into the atmosphere using three-way stopcock 53. Whenever it is desired, stopcock 53 may be turned to direct the steam into the retort. In the event that the sample should prove to be too compact to allow rapid penetration by the steam, thus building up pressures in the steam generator, the safety tube will permit the release of the pressure to the atmosphere. In using an outside steam generator, however, it is impossible to determine the amount of moisture present in the original bit cutting in one operation, since there is no measured quantity of water converted to steam. In the event that the analysis is to be set up on a "dry basis" it will be necessary to make a separate determination for the amount of moisture content by any of the well-known methods on another portion of the wet drill cuttings, or the sample can be "air dried" prior to determination of the hydrocarbon content.

Figure 3 illustrates a retort that has for its advantage simplicity of construction. Line 60 leading from measuring cylinder 17 is fabricated to pass directly through female joint 61 of retort 10 and penetrate into the retort a limited distance. By opening stopcock 62 in line 60 water is added directly from cylinder 17 to the retort. Since the retort is at an elevated temperature, the water is vaporized, flushing out the hydrocarbons still remaining within the sample. A variation of this type of retort is shown in Figure 4 which is designed to give a bottom steam delivery. The water delivery tube 60 has been lengthened to extend almost to the bottom of the retort passing through a sleeve 63 and perforated plate 64. The sample is placed in the annular space between sleeve 63 and the retort wall and on top of the perforated plate. Water injected through water tube 60 will strike the heated re-

tort bottom and instantly become vaporized, and pass upward through a perforated plate to sweep all vapors from the sample and the retort.

It is recognized that in order to add water from a cylinder such as a graduate, sufficient head must be provided to overcome the pressure exerted by the carbon tetrachloride. Ordinarily it is a simple matter to raise a water storage cylinder to a sufficient elevation to provide this required head. On the other hand, if the elevation is so great that reading the water level in the storage cylinder 17 is difficult, the alternative arrangement shown in Figure 5 can be used. Water stored in an elevated storage vessel 80 is admitted via line 81 to flask 82 by opening stopcock 83. The rising water level in flask 82 will provide an air drive to measuring cylinder 17 through stopcock 84 and line 85. Stopcock 84 is turned to provide a direct passageway from flask 82 through line 86 to line 85, meantime shutting off any passageway between line 81 and line 85 through line 87. Cylinder 17 is provided with a stopper through which line 85 enters and a release line 88 equipped with a clamp 89 or other means for closure. Whenever the flask 82 becomes filled with water from line 81, it can be drained by closing stopcock 83 and by opening clamp 89 in line 88 and drain 90. The water in cylinder 17 can be replenished at will by closing stopcock 83, opening clamp 89, and turning stopcock 84 ninety degrees clockwise so that a direct passage is formed between lines 85, 87 and 81. By using this arrangement measuring cylinder 17 can be placed at any level convenient for reading, since the water column from water container 80 to flask 82 provides the required head to overcome the pressure exerted by the absorption medium in column 21.

Although I have described the use of my apparatus employing carbon tetrachloride as an absorption medium, it should be understood that any suitable solvent can be used, particularly those mentioned previously. In some cases, however, the solvents are lighter than water, and therefore will float above the water layer. In this event it will be necessary to withdraw the solvent and absorbed hydrocarbons from a point above the water level, or to withdraw the water prior to drawing off the hydrocarbon and solvent through line 35 to vessel 36. The necessary changes to the apparatus should be obvious, and have not been illustrated.

Prior methods of extracting hydrocarbons from samples of earth formation have been confined chiefly to leaching or to the use of Soxhlet apparatus. When using either of these methods, and particularly the leaching method, various portions of organic vegetable matter are to be found in the solvent, thus masking to some extent the true hydrocarbon content of the sample due to the presence of oil and/or gas at deeper strata. The leaching method is also deficient in that not all of the heavy hydrocarbons in the sample may be absorbed in the solvent, particularly if soil waxes are present. Using Soxhlet apparatus, the heavy hydrocarbons are recovered to a much greater extent, but the danger of loss of light hydrocarbons is much increased.

Previous methods of recovering hydrocarbons from soils and cuttings have included heating samples thereof strongly, and condensing the vaporized hydrocarbons with liquid air or liquid oxygen, no solvent being used. The volume of hydrocarbons recovered is necessarily small, and the use of liquid air, while perfectly feasible in

most manufacturing centers, may offer difficulties in the way of obtaining an adequate supply for field laboratories. Moreover, it often happens that a part of the organic vegetable matter present may be decomposed, the strong heating causing destructive distillation and giving an erroneous yield of hydrocarbons. All of these shortcomings are overcome by the use of my invention. Substantially all of the hydrocarbons present are recovered by the combination of relatively mild heating and steam flushing, the loss of light or heavy hydrocarbons is reduced to a minimum, and contamination with organic vegetable matter is practically eliminated. In addition, since it is unnecessary to dry the sample before extraction, there is a saving in time as well as elimination of loss of light hydrocarbons, and if solvents heavier than water are employed, the "water seal" effect of the water above the solvent prevents solvent loss. An additional advantage is that the water content of the sample can be determined simultaneously with that of the hydrocarbon content. Simplicity of apparatus and reagents also makes it admirably suited for field work.

Certain details, such as connections, supporting means, etc. have been omitted from the description and drawings for the sake of simplicity, and will be readily supplied by those skilled in the art wishing to practice my invention. Although I have illustrated my invention by reference to certain specific embodiments thereof, it should be realized that this is by way of illustration and not by way of limitation, and that my invention is to be limited only as set forth in the appended claims.

I claim:

1. The method for the determination of hydrocarbons in earth formations which comprises heating a sample of said earth formation sufficiently to vaporize at least a substantial part of said hydrocarbons, passing said vaporized hydrocarbons into a cooled water immiscible absorption medium whereby said hydrocarbons are absorbed, thereafter passing steam through said heated sample and into said absorption medium whereby hydrocarbons remaining in said sample are vaporized and absorbed in said absorption medium, condensing the steam in said absorption medium, and determining the amount of the hydrocarbons absorbed in said absorption medium.

2. The method for the determination of hydrocarbons in earth formations which comprises heating an undried sample of said earth formation sufficiently to vaporize at least a substantial part of said hydrocarbons together with any moisture present in said sample, passing the vapors from said heated sample into an absorption medium which is immiscible with water whereby said hydrocarbons are absorbed, thereafter passing steam through said heated sample and into said absorption medium whereby hydrocarbons remaining in said sample are vaporized and absorbed in said absorption medium, con-

densing in the absorption medium containing absorbed hydrocarbons all of the moisture and steam whereby all the water will separate from the absorption medium, and determining the amount of hydrocarbons absorbed in said absorption medium.

3. The method for the determination of hydrocarbon and moisture content in earth formations which comprises heating an undried sample of said earth formation sufficiently to vaporize at least a substantial part of the hydrocarbon and moisture constituents thereof, passing said vaporized constituents into an absorption medium whereby said hydrocarbon constituents are absorbed and said moisture is condensed, passing a measured amount of steam through said heated sample and into said absorption medium, whereby hydrocarbons remaining in said sample are vaporized and absorbed in said absorption medium and said steam is condensed, determining by difference between the total condensed water and the steam added the moisture content of said sample, and separately determining the amount of hydrocarbons absorbed in said absorption medium.

4. The method according to claim 1 in which said samples of earth formation are drill cuttings taken at spaced intervals along a well bore.

5. The method according to claim 1 in which said absorption medium has a refractive index substantially different from that of the hydrocarbons from said earth formation whereby the hydrocarbons absorbed in said absorption medium are determined by comparison of the refractive index of said absorption medium and the refractive index of said absorption medium containing said absorbed hydrocarbons.

6. The method according to claim 1 in which said absorption medium is carbon tetrachloride.

7. The method according to claim 3 in which said steam is formed by vaporizing a measured quantity of water.

8. The method according to claim 1 in which said sample is heated to a temperature within the range of from about 250° F. to about 600° F.

9. The method for the determination of moisture in earth formations which comprises heating a sample of said earth formation sufficiently to vaporize at least a substantial part of said moisture together with any hydrocarbons present in said sample which are volatile at such temperatures, passing vapors from said heating through a cooled absorption medium for said hydrocarbons whereby said hydrocarbons are absorbed and said vaporized moisture condensed, passing a measured quantity of steam through said sample and into said cooled absorption medium to vaporize remaining moisture and recover it by condensation, and determining by the difference between the total condensed water and the measured amount of steam the amount of moisture present in said sample.

HENRY F. STURGIS.