

UNITED STATES PATENT OFFICE

2,336,612

GEOCHEMICAL PROSPECTING

Leo Horvitz, Houston, Tex., assignor to Esme E. Rosaire, Houston, Tex.

No Drawing. Original application March 10, 1941, Serial No. 382,606. Divided and this application July 20, 1942, Serial No. 451,630

5 Claims. (Cl. 23—230)

The present invention relates to a process of geochemical prospecting.

More specifically, the present invention relates to geochemical prospecting for carbonaceous deposits, such as oil, gas, coal and the like, and for structures in which such deposits may occur by the quantitative detection of leakage from the deposits themselves and from the rocks in which they are contained. Such leakage results in a deposition in the soil of evidence of the leakage and such evidence may be detected and measured by analysis of the soil. This invention relates to the broad subject matter of application Serial No. 107,497, filed October 24, 1936, and entitled Geophysical prospecting method.

The search for oil fields by geochemistry has heretofore been conducted by seeking actual evidence of leakage from the deposits themselves. It has been found, however, that inorganic substances not heretofore regarded as being related to the deposits themselves are indicative of proximity to buried structures which may contain the sought deposits. Thus, analyses of soil samples taken near the surface of the earth have resulted in finding variable concentrations of chlorides, the variations corresponding generally with a known structure. Many other inorganic substances are similarly indicative. Actual investigation has revealed that carbonates, bicarbonates, sulfates, sulfides, halides, basicity, acidity, total acid soluble and total water soluble constituents, etc., are suitable indicators. Practically any inorganic soil constituent may be selected as the significant constituent. The soil may be examined quantitatively for cations or anions. In certain locations examination of the soil for iron yields significant data. In other locations, some other ion may prove significant and this will ordinarily be relied upon for purposes of interpretation. Usually the content of a number of inorganic constituents in soil samples from a given area is determined and ordinarily correlation between the majority of the constituents determined will be found.

An object of the present invention is to provide a method of geochemical prospecting for buried structure capable of containing valuable deposits by the examination of surface and near surface soils for evidence therein of anomalous mineralization and secondary salt deposition.

Another object is to provide a rapid, low cost reconnaissance method of geochemical prospect-

ing which may economically be employed to evaluate large areas relative to future exploration programs.

Usually, the halo phenomenon originally observed in connection with analyses for the content of the lighter hydrocarbons and described in a paper by E. E. Rosaire, entitled, "Shallow Stratigraphic Prospecting over Gulf Coast Structure," *Geophysics* III 2, March 1938, is also observable in the technique of the present invention.

It has been observed with respect to halides, which will usually be chlorides, that the pattern obtained sometimes shows high concentrations in the samples above the producing area rather than in the samples forming a fringe or halo around the producing area. Thus, when a halide profile is obtained having a single hump rather than the double hump, which usually characterizes a profile which is taken across an area which yields the halo pattern, it will be found that the hump on the halide profile will fit in the low space between the double hump on the profile shown by hydrocarbons and other constituents. On infrequent occasions this departure from the conventional pattern is also found in sulfates, which as a rule give the conventional pattern. This deviation in pattern emphasizes the desirability in practice of analyzing the soil samples over a given area for a plurality of constituents so that the anomalies appearing in the patterns resulting from the individual constituents can be compared and interrelated to produce a complete picture of the area.

In some areas it has been found that certain constituents do not yield distinctive patterns. Usually this failure to give a pattern over a producing area will be confined to one inorganic constituent and the characteristic pattern will be shown by any number of other constituents which may be determined. Thus, in prospecting according to the present method it would be unwise to condemn an area because one inorganic constituent failed to give a characteristic pattern, but the patterns of other constituents should be obtained so that it can be determined whether or not a significant pattern is obtained with the majority of the constituents. Even if a significant pattern is obtained with only one constituent, which would indeed be a rare case, further exploration of the area by the hydrocarbon technique would be in order.

Generally, it has been found that the consistency of results is better in samples of soil taken at a depth of several feet since topsoil samples are affected by leaching by meteoric waters, local fertilization, and the like. A compromise between the economy demanded by a reconnaissance method and the reasonable accuracy demanded by any exploration method indicates that a preferred form of the invention is practiced by the collection of samples from a depth of about ten feet, though, of course, the depth may be varied depending upon general conditions of climate, nature of soil, vegetation and agricultural utilization. It will be understood that all samples in a given area should preferably be collected at the same depth.

In actual practice the soil samples are collected at the same depth over a given area where this is possible. In some areas where there are outcroppings of rock or other natural impediments it often happens that the sampling depth selected cannot be continued throughout the whole area. For example, where samples are taken at eight feet at the start, it might develop later that in some certain spot it is only possible to penetrate six feet. In such cases it is preferred to take the majority of samples at the depth originally selected and take the remaining samples at as great a depth as they can be obtained. In any case, the depth at which each sample is taken is noted on the sample container for the information of the interpreter.

The practice is often followed of determining the variation with depth of the significant constituent in the sample holes at selected points along a profile. For example, in scattered holes in the area under investigation, samples are taken at one or two foot intervals in the sample hole so as to determine the variation of the significant constituent with depth. Then if all the deep samples over the area cannot be secured at the selected depth, say 12 feet, the depth determinations will aid the operator in deciding at what depth less than 12 feet he can safely take samples where they cannot be obtained at 12 feet.

Where there is already a producing well in an area under investigation it is advantageous to make depth determinations in each sample hole along a profile passing through the well. In this way the best depth at which to collect samples in the other profiles over the area in order to outline the field can be determined.

Where there is not excessive dipping of the formations it leads to uniformity to collect the samples out of the same formation so that the samples will have, as nearly as possible, the same general nature. Ordinarily strata near the surface have such a small dip that collection of the samples at a uniform depth will result in collection of the samples in the same stratum. Should it transpire that, where the samples are being analyzed for a constituent, such as calcium, and during the collection of the samples a deposit high in calcium, such as limestone, is encountered, the operator will naturally take this into account and the large increase in the calcium content in samples taken in this deposit will be taken into consideration in the interpretation of the results.

The actual analysis of the selected soil samples may follow any acceptable quantitative procedure, the following table serving as examples. It should be remarked, however, that the table is exemplary only and should not be construed to define the scope of the invention.

Analyses

1. Halides:

- a. Leach (or extract) with (distilled) water; (refluxing known weight of soil with any volume of H_2O).
- b. Measure the H_2O extract.
- c. Titrate with standard $AgNO_3$ solution using potassium chromate (K_2CrO_4) as an indicator.

2. Bicarbonates:

- a. Heat and dry sample.
- b. Heat at higher temperature below decomposition temperature of carbonates, say $300^\circ C$. to decompose bicarbonates.
- c. Measure CO_2 evolved; or titrate with standard HCl to phenolphthalein end-point, and then titrate to methyl orange end-point. Where samples show negligible quantities of soluble carbonates, titration to phenolphthalein end-point may be omitted.

3. Soluble sulfates:

- a. Extract with distilled water.
- b. Add excess $BaCl_2$ to extract to ppt. SO_4 and titrate unused $BaCl_2$ with Na_2CO_3 , using phenolphthalein as indicator; or
- c. Titrate water extract with $BaCl_2$ using tetra-hydro-quinone as indicator.

4. Sulfitcs:

- a. Titration of water extract with standard potassium iodate and KI mixture, starch indicator.

5. Acidity (and basicity):

- a. By titration or pH measurements.

6. Water soluble constituents:

- a. Extract with distilled H_2O ; evaporate extract to dryness. Weigh residue.

7. Acid soluble constituents:

- a. Extract with acid; evaporate extract and weigh residue.

8. Carbonates (and bicarbonates):

- a. Decompose with acid and measure CO_2 evolved by volume or weight.

9. Sulfides:

- a. Decompose with acid and measure the evolved H_2O as by precipitating the sulfide of a selected metal from a solution of one of its salts and weighing the precipitate.

The constituent selected for determination will usually occur as a minor constituent of the soil sample, and may be present only in minute amounts. In some areas, however, the constituent selected as the significant constituent may constitute a very substantial portion of the soil sample. For example, in one area in which the samples were collected from caliche deposits and the variations in acid-soluble constituents, largely carbonates, were determined, an anomaly was obtained on the basis of the acid-soluble content which corresponded substantially with the anomaly prepared by analyses of samples for hydrocarbons. In many of these samples the acid-soluble components constituted more than 50% by weight of the sample. It is preferable to examine the samples for those constituents which are readily soluble in water or common inorganic acids.

A feature of considerable importance of the present invention is the discovery of the fact that in soil samples containing carbonates, it appears that the carbonates envelope not only organic matter but also inorganic compounds. For example, when it is desired to analyze soil samples for chlorides, ordinary extraction of the sample followed by titration, as indicated above, may reveal only negligible amounts of chlorides. If the sample is first treated with nitric acid or sulphuric acid, however, and then extracted and titrated, large amounts of chlorides may be found. Likewise, when it is desired to analyze for nitrates, it is extremely advantageous to first treat the sample before extraction with sulphuric or hydrochloric acid. It will be understood that the extraction itself can be effected with a dilute acid of the type desired. This same acid treatment is advantageous for analyses for all inorganic constituents.

The usefulness of this method has been demonstrated in practice in that when exploration has been conducted in areas also explored by other methods, the method was found to give information similar to that obtained by other methods. It is not intended to imply that it gives substantially the same information in all cases as geochemical exploration by analysis of soil samples for, say, ethane. The patterns resulting from the method of the present invention thus far bear a similarity to those resulting from the hydrocarbon technique.

Naturally, the results of the method of the present invention leave something to the judgment of the interpreter. Should the interpreter find that a particular inorganic constituent runs low for a large number of samples and then suddenly increases to a high level, which is also maintained for a large number of samples, he will investigate to determine the nature of the formations from which the samples were procured. Likewise, when the interpreter finds a single high sample among a group of low samples, he will investigate the circumstances to determine what significance, if any, should be given to this single indication.

As in established geophysical practice, where, for example, gravitational and magnetic data are used to determine the economic feasibility of further work by seismic or other more expensive methods, the present invention offers an inexpensive technique useful in ascertaining the economic feasibility of further exploration of a given area. In this respect, it is in a position to be compared directly with the torsion balance, gravity meter, magnetometer, resistivity and electric-transient method which measure indirect evidence of the presence of structure, with the data yielding a basis for economic exploitation with more expensive methods, like the seismic which measures the structure directly, or a geochemical method which measures the direct leakage products for the sought deposits.

While the method of prospecting herein disclosed can be used as the basis for a drilling program, it appears to best advantage when used as a basis for additional prospecting before drilling. These economic factors are expressed in a paper by E. E. Rosaire entitled "Tactics and Strategy of Exploration for Petroleum," III, Geo-

physics IV 3, July, 1939, pp. 155-166. Thus one species of the invention comprises prospecting over a region by the disclosed method, determining the areas which may economically be exploited by a prospecting method of higher resolving power, and further exploring the thus limited areas by such methods of higher resolving power.

The methods of higher resolving power include the seismic which under favorable conditions is capable of delineating structure favorable to the accumulation of oil and gas and the soil analysis method of application Serial No. 103,129, which is generally applicable to the problem of determining the existence and the real extent of such accumulations. The gravimetric, magnetometric, resistivity methods and the like do not fall in the class of methods of higher resolving power as they are generally conceded to be reconnaissance methods incapable of accurate and detailed structural analysis. Therefore, the term "method of higher resolving power," as used in this specification, is limited to the seismic method and the above mentioned soil analysis method with any improvement thereon.

As this invention is a surface method and contemplates surface methods of higher resolving power, prospecting with the drill, as by core drilling, is excluded from the definition of the term "method of higher resolving power."

This application is a division of my co-pending application Serial No. 382,606 filed March 10, 1941, and entitled Geochemical prospecting, which in turn was a continuation in part of my application Serial No. 304,141 filed November 13, 1939, and entitled Method of prospecting.

The nature and objects of the present invention having been thus described, what is claimed as new and useful and is desired to be secured by Letters Patent is:

1. A method of geochemical exploration for subterranean petroliferous deposits which comprises collecting samples of soil at spaced points in the area to be investigated at a depth several feet below the surface, said depth being sufficient to eliminate the effect of surface conditions, and subjecting the individual samples to an analysis for the determination of the content thereof of substances soluble in an inorganic acid whereby the contents so determined may be compared for the purpose of identifying anomalously high values thereof.

2. A method according to claim 1 in which each sample is extracted with an inorganic acid and the extract is evaporated to dryness and the residue weighed.

3. A method according to claim 1 in which the samples are taken at laterally spaced points and at a substantially uniform depth.

4. A method according to claim 1 in which the samples are taken at laterally spaced points and at a substantially uniform depth and each sample is extracted with an inorganic acid and the extract evaporated to dryness and the residue weighed.

5. A method according to claim 1 in which the samples are taken at laterally spaced points and at a depth of at least ten feet.

LEO HORVITZ.