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GEOCHEMICAL PROSPECTING

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The present invention is directed to geochemical prospecting including the geochemical logging of bore holes for subterranean petroliferous deposits.

In my co-pending application Serial No. 305,063, filed November 18, 1939, now Patent 2,278,929, issued April 7, 1942, I have disclosed a method of geochemical prospecting according to which the presence of subterranean petroliferous deposits is manifested by the presence in soil samples of free metals which are determined by measurement of hydrogen evolved when the samples are treated with acid. In said copending application I have disclosed a method of treating the soil samples according to which the sample is treated with a mineral acid such as hydrochloric acid to produce an extract and then this extract is titrated with $K_2Cr_2O_7$ or $KMnO_4$. The result will be the content of free and ferrous iron. This present application is a continuation in part of said co-pending application.

An object of the present invention is to provide a prospecting method applicable to deposits subject to leakage, the leakage products of which are hydrocarbons and their derivatives which provide a reducing influence.

Thus, a further object of this invention is to determine in the earth's crust the valence of metals which have a plurality of valencies, i. e. are polyvalent, for the purpose of indicating the presence and location of deposits the vapors of which are of a reducing nature.

Another object of the present invention is to determine the free metals and -ous ions of metals which normally exist in the -ic state; that is to say, to determine free metals and ions existing in reduced state of polyvalent metals, the normal occurrence of which is the higher or highest valence state.

The present invention is based on the discovery that the quantity of iron present in the soil in the ferrous state is a significant indicator of petroliferous deposits. This is true in surface prospecting as well as in well logging. It is understood that in surface prospecting the samples are preferably collected at laterally spaced intervals and at a uniform depth, usually below ten feet, while in well logging the samples are collected as cuttings or cores at various depths during the progress of drilling.

It would have been expected that the ferrous content of the soil in a region through which hydrocarbon gases had diffused would show variations corresponding to those obtained when the soil is treated with an acid and the evolved hydrogen measured. It would naturally be assumed that any free metal present is produced by reduction which would also be the action which would account for the presence of ferrous iron. Surprisingly enough, however, the logs produced by analyses of samples for ferrous iron do not correspond with the logs produced by the analyses of samples for hydrogen evolved by treatment of acid, but conform to the hydrocarbon logs obtained in accordance with previous applications.

Many logs have been run on wells which were later completed, and the following significant patterns recognized.

In a producer the log for hydrogen shows low values near the top of the hole, increases to a maximum before the producing horizon is reached, and then decreases to negligible values near the producing horizon. The hydrocarbon log shows low values near the top and values which increase more or less steadily to a depth near the producing horizon where they increase very rapidly to production. The well log of the ferrous iron shows the same type of pattern as the hydrocarbon log.

In the case of a dry hole, the hydrogen log never reaches a well defined maximum, and the hydrocarbon log shows little or no tendency to increase with depth. Patterns of well logs for wells near the center of production, inside and outside the edges and remote from production, have been studied and in all cases the ferrous iron log exhibits the same pattern as does the hydrocarbon log.

In surface prospecting maps of ferrous iron concentration show substantially the same patterns as do maps of hydrocarbon concentration. Iron seems to be generally present in combined form at the surface, and its presence in the ferrous state is significant.

Why the ferrous iron fails to show the same pattern in a well log as hydrogen (see copending appliaction Ser. No. 310,358, filed December 21, 1939), has not yet been satisfactorily explained. This is a peculiar fact, but one which is valuable because a well may be logged for inorganic constituents and conclusions reached which are substantially as useful as those reached from a well log made in accordance with the above mentioned patent application Serial No. 310,358.

In the practice of the present invention in geochemical prospecting the surface soils or well cuttings are first dried so that the weight of the moisture-free sample can be measured. This step may be omitted if the moisture content is determined using a separate portion of the sam-

ple. The sample is mixed with concentrated hydrochloric acid. Any strength acid may be employed, but in practice the concentrated solution is used. It will be understood that the amount of acid used in measured quantitatively. An aliquot portion of the acid extract after separation from the residue is then titrated in a known manner for ferrous iron.

It will be understood that the determination of the iron can be made in other ways known in the art. However, the volumetric method is the method desirable. As is known, this method consists in first adding to the acid extract a preventive solution, made up of a mixture of manganous sulfate, sulfuric acid and and phosphoric acid, and then titrating with standardized potassium permanganate solution.

In the practice of the present invention it is desirable to also measure the total iron present and thereby determine by difference the amount of ferric iron. This is simply done by adding zinc to an aliquot portion of the acid extract so as to convert all the combined iron to ferrous iron and then titrating the extract as above described. The difference between the total iron and the ferrous iron represents the ferric iron in the sample.

In surface prospecting it is usually preferable to plot on a map the ratio of ferrous iron to total iron in the soil. In well logging, however, it is usually preferably to draft logs by plotting the ferrous iron in percent of total sample. As has been previously indicated, in well logging the ferrous iron log generally conforms quite accurately with the hydrocarbon log. However, there is one difference between them which is quite significant. A well drilled off the edge of the field, but still close enough to the field to have shows of hydrocarbons will yield a hydrocarbon log which, to a substantial depth, will have an appearance of a log of a well approaching a producing formation. The ferrous iron log, however, affords a warning in such cases in that the ferrous iron shows high values at the surface and then, usually at a depth of only about 1000 feet, decreases to small quantities and thereafter builds up slowly to a more or less constant value which value is much smaller than that shown near the surface.

If it is desired to make a correction for the free iron present, the soil sample may be first treated with a solution of copper sulfate. Any free iron will go into solution and the extract removed by filtration. The water soluble ferrous compounds present in the soil are usually negligible in quantity, so the extract contains substantially only iron originally present in the free state and the soil sample still contains the ferrous iron. The copper sulfate extract, titrated in the usual manner for ferrous iron, yields the value of the free iron. The soil residue may then be treated with acid and the acid extract titrated as described above for the ferrous content.

It is preferable to use aliquot portions of soil for the ferrous and free metal determination, as outlined immediately above. One portion is treated with the copper sulfate and the thus obtained extract is titrated for ferrous iron, this data yielding the free iron originally present in the soil. The other aliquot portion is acid treated to solubilize both the free and combined iron. The extract thus formed is titrated for ferrous iron, the result yielding the value of the ferrous plus free iron. The ferrous content alone may then be found simply by deducting the free iron.

The total iron may be determined by extracting still another aliquot portion wtih acid, reducing any ferric iron present and titrating for ferrous iron. The ferric content may be determined by deducting from the value of total iron found the values of ferrous and free iron.

Magnetite (Fe_3O_4 or $FeO.Fe_2O_3$) is fairly stable and may have been formed elsewhere than at the point at which the samples were collected. This soil constitutent may be removed with a magnet before running the ferrous tests. Such magnetic treatment also removes free iron, but the significant of the test for ferrous iron is not disturbed. The removal of magnetic material including free iron is evidently quite nearly complete, as aliquot portions of samples yielding high hydrogen after magnetic treatment yielded negligible hydrogen.

In the practice of the method of the present invention for surface prospecting the samples of soil to be analyzed are collected systematically according to any desired pattern over the area to be prospected. It is somewhat surprising that in this particular case samples need not be collected at any substantial depth, but can be collected along the surface itself after the surface vegetation has been scraped away. Of course, judgment must be exercised in collecting the samples, and where the surface has been recently disturbed as by cultivation, or where the surface is exposed to adverse influences, such as treatment with fertilizing agents and the like, it will be desirable to collect the samples at depths below the influence of such surface disturbances. It is preferred that the samples are collected at depths of four feet and greater, such as below the water table, say between ten and twenty feet, and to collect all the samples at the same depth. Variations in the depth of collection, however, are permissible and in some cases, by reason of the nature of the terrain, necessary.

When the method is applied to well logging, the samples used may be either cores cut for the purpose, or cuttings which come to the surface during the drilling operation. As is the custom in paleontology, these cuttings are correlated with depth by taking into consideration the velocity of the drilling fluid as well as the rate of penetration of the drill bit.

Throughout the specification, reference has been made to ferrous iron. Manifestly, the method can be extended to the use, as an indicator, of the -ous ion of any polyvalent metal which normally exists in the -ic state, and which is reduced to the -ous state due to the presence of the reducing hydrocarbons. Stated another way, the method is applicable by using as an indicator the presence and quantity of ions of lower valence states of polyvalent metals.

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

1. The method of geochemical prospecting for deposits the leakage components of which are of a reducing nature comprising collecting earth samples at spaced points in a region to be explored, analyzing such samples for those ions of a polyvalent element the -ic oxide of which is reducible by hydrocarbon gases, present in lower states of valence and correlating the values determined with sample locations whereby infor-

mation indicative of the presence of such deposits is obtained.

2. The method of geochemical prospecting for petroliferous deposits comprising collecting samples of soil at spaced points in an area to be examined, analyzing them for -ous ions of a metal the -ic oxide of which is reducible by a hydrocarbon gas and the normal occurrence of which is the -ic state and correlating the values determined with sample locations whereby information indicative of the presence of such deposits is obtained.

3. The method according to claim 1 in which the samples consist of cuttings collected from a well in the process of drilling.

4. The method of geochemical prospecting for carbonaceous deposits comprising collecting samples of soil at a uniform depth in a systematic manner at spaced points over an area to be explored, analyzing them for the presence of ions of a metal, the -ic oxide of which is reducible by a hydrocarbon gas, in a state of valence lower than the state of valence normally encountered in nature and correlating the values determined with sample locations whereby information indicative of the presence of such deposits is obtained.

5. The method of geochemical prospecting for carbonaceous deposits comprising collecting samples of soil at spaced points in an area to be explored, and analyzing such samples for ferrous ions and correlating the values determined with sample locations whereby information indicative of the presence of such deposits is obtained.

6. The method of geochemical prospecting for carbonaceous deposits comprising collecting samples of soil in a systematic manner at spaced points in an area to be explored, determining the relative amounts of ions of higher and lower valence of a polyvalent metal, the -ic oxide of which is reducible by a hydrocarbon gas, contained in said sample which normally occurs in its highest valent state and correlating the values determined with sample locations whereby information indicative of the presence of such deposits is obtained.

7. The method in accordance with claim 5 characterized in first removing free iron and magnetite from the samples before determining the ferrous content.

8. In a method of prospecting for carboneceous deposits by collecting samples of soil over an area to be explored and analyzing such samples for their content of a metal, the -ic oxide of which is reducible by a hydrocarbon gas, in states of valence lower than the most highly oxidized state, the steps comprising extracting each sample with a solution of a salt, the metallic radical of which is displaceable by the sought metal in metallic form and the acid radical of which forms soluble salts of said sought metal, removing the extract so formed from the soil residue, further treating the soil residue with an acid to solubilize the salts of the sought metal to form an extract thereof, determining the amount of reduced valence ions of said sought metal in said second extract whereby the values determined may be correlated with sample locations.

9. The method according to claim 8 in which the sought metal existing in the free state in the original soil sample is determined by analyzing for ions of said sought metal in the first extract.

10. The method according to claim 8 in which the metal is iron, the salt is selected from the group comprising copper sulfate and silver nitrate, and the sought ions have a valence of 2.

11. The method according to claim 8 in which aliquot portions of said second extract are analyzed respectively for ions of the sought metal in a lower valence state and for ions of said metal in the highest valence state.

12. A method of logging a borehole drilled for petroleum which comprises collecting samples of the formations penetrated at spaced points along the borehole, analyzing said samples for those ions of a polyvalent element, the -ic oxide of which is reducible by a hydrocarbon gas, present in lower states of valence and correlating the values determined with sample depths whereby information indicative of the approach of the borehole to petroleum may be obtained.

13. A method of logging a borehole drilled for petroleum which comprises collecting samples of the formations penetrated at spaced points along the borehole, analyzing said samples for their contents of ferrous iron and correlating the values determined with sample depths whereby information indicative of the approach of the borehole to petroleum may be obtained.

14. A method according to claim 13 in which the samples analyzed are cuttings obtained during the drilling operation.

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