



## A COMPARISON OF SURFACE GEOCHEMICAL TECHNIQUES

### Summary

Vertical migration of volatile compounds from oil and gas reservoirs can be sensed using surface geochemical techniques. For more than 75 years, geologists exploring for oil & gas have developed and tested such methods which can image petroleum reservoirs by measuring near surface parameters. Traditional techniques have included direct soil analysis, active soil gas measurement, and microbial techniques. Unfortunately, these traditional methods suffer from some limitations. These include poor absorbance of soils at a high percentage of sample sites, sampling difficulty due to poor soil permeability, low analytical sensitivity, limited data sets of C<sub>1</sub>-C<sub>5</sub> hydrocarbons (methane-pentane), problems resulting from variability in the site soil and meteorological conditions, and interference from biologically generated methane. For these reasons, such techniques offer are of limited utility and hence limited value.

A revolutionary technique has been developed by Amplified Geochemical Imaging LLC (AGI), known as AGI Survey for Exploration. This technique overcomes the shortcomings of other methods and when combined with other exploration tools, greatly reduces risk and enhances exploration success. The technique makes use of a sampler with engineered hydrophobic adsorbents encased in tubular membrane material. The sampler is deployed into the ground for ~20 days, and is analyzed using custom thermal desorption GC/MS instrumentation with measurement sensitivity in the *ppt* range. Resulting geochemical data is evaluated using multivariate statistical interpretation techniques. Upstream exploration groups who have evaluated all of the available geochemical techniques have found the AGI Survey method to be reliable and of high value for their exploration programs.

### Vertical Migration of Hydrocarbons

All near-surface methods rely on documented physical phenomena of vertical *microseepage* of hydrocarbons from the reservoir (Klusman, 1996). This is different from *macroseepage* where a reservoir is breached and hydrocarbons flow along discontinuities in the stratigraphic section. With *microseepage*, an effective reservoir seal is still present but reservoir pressure and high hydrocarbon concentration create a natural driving force through the seal. Hydrocarbons move from high concentration and pressure in the reservoir toward low concentration and pressure at the surface of the earth. While the reservoir seal is effective in holding 99+% of the hydrocarbons in the reservoir, the seal is not completely impervious, with grain boundaries and microfractures through the overburden as pathways for the upward movement of the hydrocarbons.

The physical mechanisms which aid in driving these hydrocarbons toward the surface at rates on the order of meters/day include:

1. Buoyancy: relative density differences between hydrocarbons and water or soil;
2. Gas entrainment: gases rising toward the surface which carry hydrocarbons.



## Direct Analysis of Soils

In the direct analysis of soils, a soil sample is collected over the site and bound hydrocarbons typically in the C<sub>1</sub>-C<sub>5</sub> (methane-pentane) range, are measured. This technique has the advantages of simplicity in collection and analysis and is relatively inexpensive. However there are four major shortcomings of this method:

1. Many soil types are very poor collectors of hydrocarbons due to lack of organic content, mineral types, pH, and other soil parameters (Conant *et al.*, 1996; Pignatello and Xing, 1996). In studies of C<sub>13</sub>/C<sub>12</sub> isotopes, soils of only 1 in 5 exploration sites had the minimum required nano-mole (12 nanograms) of hydrocarbons required for this analysis. Most direct soil analysis techniques require orders of magnitude more bound hydrocarbon than this. Thus few exploration sites will favor this technique simply because the soils are not good hydrocarbon collectors. In addition, over medium to large exploration sites, soil characteristics and absorbance can vary dramatically making it difficult to identify patterns conforming to the reservoir;
2. More than 50% of hydrocarbons in soil may be lost during sampling due to volatilization during soil handling (Hewitt and Lukash, 1996);
3. Analytical techniques used to measure hydrocarbons in soil are not very sensitive. Values in micrograms (10<sup>-6</sup> grams) are typical;
4. This technique is generally limited to finding only C<sub>1</sub>-C<sub>5</sub> hydrocarbons. This is a rather limited data set when exploring for dry gas, but particularly for wet gas, condensate or oil reservoirs. Additionally, some of this compound range (methane in particular), is often generated by near-surface microbial activity and thus may not reflect reservoir migration.

In summary, direct soil analysis while simple and relatively inexpensive, has limited utility due to poor soil absorbance, lack of measurement sensitivity, limited hydrocarbon data sets, and interference by near-surface methane generation.

## Active Soil Gas Measurement

With active soil gas measurements a shallow hole is made in the ground and a sample of gases contained within the soil (not hydrocarbons adsorbed onto the soil) is extracted via a probe inserted in the hole. Gases are then analyzed for C<sub>1</sub>-C<sub>5</sub> compounds typically. As with soil samples, this method has the advantages of easy collection (except in bedrock), easy analysis, and relatively low cost. However, the technique suffers from some of the same limitations as soil analysis; namely, collection problems, poor sensitivity, limited compound range, and interference from surface biological methane generation. To be specific:

- The most significant limitation of active soil gas collection is the difficulty, or in some cases, impossibility of drawing a gas sample from the ground (e.g., clay-rich soils with low permeability, rock outcrops, or water saturated soils) (Klusman, 1993). Even in soils with some permeability, it can be difficult to seal the extraction probe to the hole resulting in a sample diluted by simultaneous draw of ambient air. As with soil sampling

over medium to large exploration sites, soil permeability and water saturation can vary significantly resulting in data variance and potential bias which will inhibit the imaging of the reservoir.

- Active soil gas sampling is also influenced by atmospheric changes and solar heating. Because the active drawing of a soil gas sample represents a single point in time, low pressure fronts moving through the area prior to the sampling will yield low concentrations as the front pulls the soil gas into the atmosphere. Likewise, soil gas concentrations vary significantly during the day as the sun heats the surface of the earth creating a thermal pump. It becomes difficult to compare results of samples taken on different days or even different hours of the day due to these meteorological variations.
- As with soil analysis, active soil gas suffers from poor sensitivity (*ppm* range typically), and limited hydrocarbon range of C<sub>1</sub>-C<sub>5</sub> at best. It is also impacted by near surface biologically produced methane and other light gases.

In summary, active soil gas measurement has limited utility in exploration due to sampling difficulty in low permeability soils, effects of solar heating and atmospheric pressure variations, low sensitivity to a narrow range of hydrocarbons, and the influence of near-surface biologically generated compounds.

## Microbial Analysis

With microbial analysis, soil samples are collected over the exploration site typically from <1 meter beneath the surface. Here the interest is measuring the mass of microbes in the soil that have been growing on light gases in the soil. With some variations in process details, microbial methods involve culturing naturally occurring microbes in soil samples with light hydrocarbon gases under laboratory control; alternatively, microbes are cultured on an agar of n-butanol. Microbial colonies are counted after a prescribed time (Klusman, 1993). This bacterial “count” is used as an indirect indicator of the concentration of hydrocarbons that had existed in the soil (presumably by microseepage). This is a relatively inexpensive method, with several concerns of note:

- The most serious limitation of microbial sampling and analysis is its indirect nature. There is no attempt to measure actual hydrocarbon compounds in the soil, rather only the bacterial count which may be proportional to or represent in some fashion the concentration of light hydrocarbons in the soil.
- Another almost equally serious limitation relates to the generated data set. By feeding either specific light gases or n-butanol, the culture favors microbes that thrive preferentially on a few compounds, for example C<sub>4</sub> (n-butane). Thus the result is not only indirectly related to vertical migration from the reservoir, but consists of only a single value per sample that may relate most specifically to soil exposed to C<sub>4</sub>. Such a limited data set precludes any robust multivariable analysis.

- A third serious limitation with microbial techniques is identical to that of soil analyses, namely that most soils are poor collectors of hydrocarbons, and will vary significantly over medium to large exploration sites. It seems little effort is taken to normalize the effects of soil variability in resulting microbial analyses. This is further complicated in very dry environments such as deserts, where despite available hydrocarbons the soil moisture content is inadequate to support microbial communities.

In summary, microbial techniques, although one of the least expensive surface geochemical techniques, has significant limitations due to its indirect nature, the univariate data set ( $C_4$  content, or bacterial count), its limited utility in about 1 of 5 sites where soil is a reasonably adsorbent, and the inhomogeneous nature of soils throughout a typical survey area.

### **An Advanced Method – Passive Sampling**

After examining the disadvantages of direct soil analysis, active soil gas collection, and microbial methods, the reluctance of the petroleum exploration industry to accept surface geochemical techniques is easier to understand. Sufficient hydrocarbons for reliable measure in <20% of sample sites, limited data sets with poor predictability, poor sensitivity, and variances in soil character over the survey areas – there are several reasons for which geochemical interpretations have suffered. Even though these techniques may be relatively inexpensive, their value is too limited to be cost effective.

After examining the deficiencies of these early surface geochemical techniques, a different approach was taken in development of a surface geochemical method which eliminates or minimizes the afore-mentioned limitations. A sample system is now available which uses selected adsorbents for consistent hydrocarbon compound collection, passive sampling protocol allowing for longer term sample collection, and high sensitivity GC/MS analysis for compound-specific measurement in the *ppt* range. Basically, improvements have been pioneered in four areas:

1. A sample collector designed to eliminate problems with soil absorbance and extraction, by providing consistent ability to adsorb *in situ* hydrocarbons;
2. Time-integrated sampling method which eliminates certain negative effects such as poor soil condition, soil heterogeneity, and varying ambient weather conditions;
3. A greatly improved analytical method which extends hydrocarbon compound measurement to well beyond the  $C_1$ - $C_5$  range of active and soil methods, and significantly increased sensitivity allowing the detection of reservoir hydrocarbons even through thick sequences of volcanics and evaporates;
4. Multivariate data processing techniques, developed to utilize this robust geochemical data and improve the imaging of petroleum reservoirs of all types.



## The AGI Survey for Exploration

To eliminate such problems as soils having limited capacity for hydrocarbon retention AGI has engineered a hydrophobic adsorbent sample specifically to collect C<sub>2</sub>-C<sub>20</sub> hydrocarbons. While compounds don't need to be gases to have a measurable vapor pressure and exist as a component of soil gas, hydrocarbons greater than C<sub>20</sub> typically have vapor pressures too low for molecules to be found in the gaseous state. The adsorbent's hydrophobic nature minimizes competition with water vapor at sample sites with high relative moisture content. Because some exploration surveys may include both dry and saturated (swampy) areas, the hydrophobic nature of the engineered adsorbent sample is critical for consistent sample measurement across a survey region. The adsorbents are sealed inside a tube of microporous expanded polytetrafluoroethylene (ePTFE), more commonly known as GORE membrane. This membrane has micropores of size so as to keep out water to depths of 25-50' yet allow free diffusion of gases onto the encased adsorbents.

The AGI geochemical sample is easily deployed by inserting it into a narrow diameter hole drilled into the ground to depth of ~0.6 – 0.8 meters. Field installation and retrieval of samples is easy and of low cost, allowing for economical deployment over difficult terrain with no disruption to landowners. The sample is left in the ground for a period of ~20 days, during which passive collection of volatile compounds occurs. This extended sample period eliminates potential variability due to atmospheric changes, solar heating, rain, or other meteorological events. Additionally, the longer time boosts the hydrocarbon signal on the sample by continually collecting vapors while in the ground (time-integrative sample nature).

AGI has also developed a very high sensitivity analytical method to measure hydrocarbon compound response from the sample quantitatively. Compound response is rendered in mass units, based on comparison with compound standards analyzed along with survey samples. The analytical method uses a thermal desorber to transfer compounds from the sample adsorbents directly into a gas chromatographic (GC) column. The GC column will separate each of about 90 organic compounds in the C<sub>2</sub>-C<sub>20</sub> range, so that subsequently a mass spectrometer (MS) may be used to identify and quantify each compound. The sum total of this system of engineered adsorbent sample – time integrated sampling – high sensitivity GC/MS analysis, is a method which can collect and measure hydrocarbon concentrations equivalent to ~1 nanogram (10<sup>-9</sup> grams) or ~1 part per trillion (*ppt*). This capability represents three orders of magnitude greater sensitivity than best alternative methods.

Rather than the five or so compounds from C<sub>1</sub> to C<sub>5</sub> as measured by direct or active soil gas methods, the nearly 90 compounds from C<sub>2</sub> to C<sub>20</sub> allows the AGI Survey method to differentiate between the various hydrocarbon fingerprints found naturally in soils over uncharged areas and over charged reservoirs. Further, this robust data set allows AGI to classify compound signatures from dry gas, wet gas, condensate, and oil reservoirs.

The advanced collector and higher sensitivity GC/MS analysis is important to the success of AGI Surveys in all exploration environments, including desert, forested, jungle, swampy, shallow embayment, and even frozen tundra. Geochemical surveys using this technique have been run during all seasons and numerous sedimentary basins around the world. Robust multivariate statistical techniques are employed to interpret the broad hydrocarbon data set. These techniques identify fingerprints of compounds at the surface which relate to charged reservoirs (direct reservoir hydrocarbon detection and identification). In frontier areas where petroleum system information may be lacking, AGI uses hierarchical cluster analysis techniques to identify groups of compounds which indicate basic hydrocarbon phase against regional background signatures. Depending on geochemical sample resolution, geochemical leads may be defined which are correlated to subsurface closures (prospects). When plotted on a map, these geochemical delineations of reservoirs can be integrated with other geological and geophysical information in order to maximize drilling success.

The value in use for the AGI Survey for Exploration has been validated by many hundreds of surveys throughout the world, with tracked success rates of higher than 90% in predicting dry holes within low response areas, and predicting hydrocarbon accumulations within high probability areas (Potter *et al.*, 1996).

## References

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